Efficient Preparation of Si$_3$N$_4$ by Microwave Treatment of Solar-Grade Waste Silicon Powder

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ABSTRACT: In this study, the waste silicon powder generated in the production of solar-grade polysilicon scrap was used as the raw material, and silicon nitride (Si$_3$N$_4$) was directly efficiently prepared by the microwave heating nitridation. The temperature raising characteristics of silicon powder by microwave heating and the influencing factors of the nitridation reaction process were studied. The thermogravimetric analysis was performed, and the temperature raising dielectric properties of silicon powder were studied. The electromagnetic field and temperature distributions of the microwave heating-induced silicon powder nitridation process were simulated using COMSOL software. The nitridation reaction of silicon powder induced by microwave heating has better temperature raising characteristics: the average heating rate can reach 135 °C/min, and the reaction time is significantly shortened (only 10–20 min). Microwave heating decreases the nitridation reaction temperature by more than 100 °C and greatly shortens the reaction time. With the increase of nitrogen pressure and reaction time, the nitridation reaction is better. In addition, the conversion of the nitridation reaction is more than 97%, and the products are mainly β-Si$_3$N$_4$ with the uniform and columnar morphology. Finally, it is proved that the efficient recovery and utilization of industrial waste silicon powder are realized, and there is lower energy consumption by microwave heating technology.

1. INTRODUCTION

Solar power generation has the advantages of cleanliness, environmental protection, safety, convenience, and abundant resources. However, with the rapid development of solar power generation, the recycling of a large amount of cutting waste generated during the preparation of solar cells is a current research hotspot. Lin et al. recovered high-purity silicon powder by different methods from cutting waste. A new idea that uses solar-grade polycrystalline silicon cutting waste to produce special ceramics realized the comprehensive utilization of cutting waste and increased the added value of the product. Si$_3$N$_4$ products are receiving more and more attention because of their excellent physical and chemical properties, such as high-temperature strength, thermal shock resistance, oxidation resistance, abrasion resistance, and self-lubrication. These products have been used in the manufacturing of high-temperature components of gas engines and filters, high-temperature ceramic bearings, thermal insulators, corrosion- and wear-resistant components in the chemical industry, and high-speed cutting tools, with broad application prospects. Si$_3$N$_4$ powder is the primary raw material of Si$_3$N$_4$ products; its preparation is an essential topic of current research, which has been widely considered.

At present, the preparation methods of silicon nitride powder mainly include the direct nitridation method, the carbothermal reduction method, the self-propagating high-temperature synthesis method, the chemical vapor deposition method, the sol–gel method, and the silicon-imide thermal decomposition method. Wang et al. prepared Si$_3$N$_4$ powder with higher purity by preheating-assisted combustion at low N$_2$ pressures. Ye et al. prepared the yttrium aluminum garnet (Y$_3$Al$_5$O$_{12}$) precursor-coated Si$_3$N$_4$ powder using the urea homogeneous preparation technique, in which urea was used as a precipitant. Arik et al. synthesised Si$_3$N$_4$ from sepiolite by the carbothermal reduction and nitridation process. Weimer et al. obtained α-Si$_3$N$_4$ powder from pyrolyzed rice hulls by carbothermal reduction and nitridation process. Zhou et al. synthesised Si$_3$N$_4$ from sepiolite by the carbothermal reduction and nitridation process. Huo et al. successfully synthesized the well-crystallized pure rod-shaped α-Si$_3$N$_4$ powder by carbothermal reduction–nitridation. 

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wires from a spent Fe−Si catalyst. Wang and Wada used the carbothermal reduction of silica to synthesize Si$_3$N$_4$ nanowires. In order to obtain silicon nitride powders by conventional preparation technology, high nitridation reaction temperatures, low heating rates, and longer nitridation reaction times or high equipment conditions are required, and the high production cost limits the widespread use of Si$_3$N$_4$ ceramic materials. Therefore, some new preparation techniques are being developed, including the discharge plasma method and the microwave method. Among them, the microwave technology has attracted much attention because of its advantages of fast and uniform heating, high efficiency, and energy saving.

In this study, the preparation of silicon nitride from solar-grade waste silicon powder by microwave heating and direct nitridation was studied. The characteristics of microwave heating in the nitridation reaction of silicon powder were investigated. The thermogravimetric and dielectric properties of silicon powder were measured and analyzed, and the effects of nitridation time and nitrogen pressure on the nitridation reaction process were studied. The energy consumption of the nitridation reaction was calculated. The electromagnetic field and temperature distributions of the microwave heating-induced silicon powder nitridation process were simulated using COMSOL software.

2. RESULTS AND DISCUSSION

2.1. Thermogravimetric Analysis. To study the nitridation and oxidation behavior of silicon powder before the experiment, thermal analyses were carried out under nitrogen and oxygen, as shown in Figure 1. The thermogravimetric analysis (TGA) of silicon powder under the nitrogen atmosphere is illustrated in Figure 1a. The temperature range of test was from 25 to 1500 °C, and the heating rate was 10 °C/min. It can be seen from the thermogravimetry (TG) and derivative thermogravimetry (DTG) curves in Figure 1a that
the silicon powder exhibits a slight weight loss at lower temperatures, which might have been caused by the evaporation of water absorbed by the silicon powder. The mass is relatively stable with the change of temperature, and the corresponding conversion rate of the nitridation reaction of silicon powder undergoes little change. This indicates that the temperature is the main factor limiting the direct nitridation of silicon powder at this stage. When the temperature is higher than 900 °C, it can be seen from the TG and DTG curves that the quality of the silicon powder begins to increase slowly. This indicates that the partial nitridation reaction of silicon powder began, but the reaction rate did not increase significantly. When the temperature reached 1350 °C, the mass change curve and the mass change rate show a sudden increasing trend. The results indicate that the silicon powder undergoes intense nitridation reaction to form silicon nitride. With the temperature rising to around 1400 °C, the rate of weight gain of the sample decreased rapidly, indicating that the nitridation reaction had been basically completed.

Figure 1b shows the thermogravimetric behavior of silicon powder under the oxygen atmosphere. The initial stage is the same as under the nitrogen atmosphere. Thereafter, the phenomenon of slight weight loss occurs immediately. When the temperature rises to 600 °C, it can be seen from the TG curve that the quality of the silicon powder begins to increase slowly. It indicates that part of silicon powder began to oxidize, but the reaction rate was not significant. When the temperature was over 750 °C, the weight of the sample increased significantly, indicating that the silica powder would undergo severe oxidation. It also indicates that the oxidation temperature of the silicon powder is much lower than the nitridation temperature. Therefore, the nitridation process must be carried out in the absence of oxygen.

2.2. Determination of Raw Material Dielectric Parameters. To study the microwave absorption properties of silicon powder, the dielectric parameters of silicon powder with different densities during heating were measured. As illustrated in Figure 2, the test temperature range is from room temperature to 1000 °C. Figure 2a–c presents the relative dielectric constant, the relative dielectric loss factor, and the dielectric loss tangent, respectively. Generally, the dielectric loss tangent is the main parameter to show the absorption of microwave energy and its conversion into thermal energy. As shown in Figure 2, the relative dielectric constant, the relative dielectric loss factor, and the dielectric loss tangent of silicon powder range from 1.0 to 6.0, 0.1 to 1.0, and 0.1 to 0.2, respectively. With the increase of the test temperature below 600 °C, the relative dielectric constant and the relative dielectric loss factor of the silicon powder changed very slightly, and the dielectric loss tangent increased significantly. This indicated that the silicon powder had excellent ability to absorb microwaves, and could be heated by microwaves. When the temperature increased from 600 to 800 °C, the relative dielectric constant and the relative dielectric loss factor increased rapidly with the increase of temperature. Then, with the continuous increase in temperature, the trend remained unchanged or decreased. However, the dielectric loss tangent increased rapidly after 600 °C, reached its maximum at 750 °C, and then decreased rapidly. It can be seen from the dielectric parameter test that the properties of the samples have changed in the temperature range of 600–800 °C. This can be proved by the rapid changes in the relative dielectric constant and the relative dielectric loss factor. Since the dielectric testing system is open, some silicon powder may be oxidized due to the increase in temperature. Especially, when the temperature is higher than 750 °C, the dielectric loss tangent decreases rapidly because of the severe oxidation reaction of silicon powder. Therefore, the microwave absorption capacity of the sample was reduced. In addition, the relative dielectric constant and the relative dielectric loss factor increased with increasing silicon powder density, while the dielectric loss tangent did not change significantly below 600 °C. However, the dielectric loss tangent of high-density silicon powder was more significant in the temperature range of 600–750 °C. This may also indicate that the oxidation rate of silicon powder decreases under dense conditions, and it still has good microwave absorption ability until 750 °C. These results were consistent with the TGA in the oxygen environment, as illustrated in Figure 1b.

2.3. Temperature Raising Characteristics of Microwave Heating during the Nitridation Process of Silicon Powder. Figure 3 illustrates the heating curves of 100 g of silicon powder under different microwave powers operated under the nitrogen atmosphere. It can be seen from Figure 3 that microwave heating of silicon powder has better temperature raising characteristics, and the heating rate increases significantly with the increase of microwave power. First, 1350 °C was set as the target temperature of the experiment. When the microwave power was 1500 W, it took 58 min to heat the silicon powder to 1350 °C, and the average heating rate was only 23 °C/min. When the microwave power was 2000 W, it took 30 min to rise to 1350 °C, and the average heating rate was about 45 °C/min. This is consistent with the result of Xu et al.39 Furthermore, when the microwave power was 2500 W, 5836
the heating rate of silicon powder increased rapidly, and the time to raise the temperature to 1350 °C was only approximately 10 min. The above average heating rate could reach 135 °C/min, while the heating rate of the conventional heating method was 5–10 °C/min. Therefore, microwave heating is significantly faster than the traditional heating methods, and it dramatically shortens the processing time.

The process of nitridation reaction is a fast-changing dynamic process. It is difficult to simulate and calculate the effect of silicon nitride formation on the distribution of the microwave electromagnetic field and the change in the heating process. Therefore, we only simulate the temperature rise process of silicon powder. COMSOL software was used to simulate the electromagnetic field and temperature distribution in the nitridation process of microwave heating of silicon powder, as shown in Figure 3. Figure 3a shows the actual heating curve and the simulated heating curve. The simulated power is 2000 and 2500 W. It can be seen from the figure that the actual heating curve and the simulated heating curve have a higher degree of fit. When the temperature exceeds 850 °C, the actual process begins to slow. This may be because the microwave absorption property of the material becomes worse when silicon nitride is formed, and the heating rate becomes slower. We have measured the dielectric parameters of silicon nitride, and the results show that the microwave absorption performance of silicon nitride powder is poor, which is consistent with that reported in the literature. Furthermore, we have also carried out an experiment of microwave heating of silicon nitride powder; the results are the same as the dielectric test, which also shows that silicon nitride powder is difficult to be directly heated by microwaves. Figure 3b shows the electromagnetic field distribution. In microwave ovens, the electric and magnetic fields are symmetrically distributed. Figure 3c shows a temperature distribution diagram. The temperature is slightly higher on the surface than in the interior, which is also consistent with the experimental results. In order to solve the problem of uneven distribution of the electromagnetic field, rotation was adopted to ensure uniform heating.

2.4. Effect of the Heating Method on the Nitridation Process. Figure 4 shows the X-ray diffraction (XRD) patterns of samples under different nitridation reaction methods and of the silicon powder raw material. The effects of conventional heating and microwave heating on the nitridation reaction were studied. First, the samples were heated to 1250 and 1350 °C by conventional heating for a duration of 20 min. The N2 pressure was maintained at around 121 kPa. It can be seen from Figure 4 that the XRD peak of the raw material corresponds to the standard diffraction peak of silicon (PDF: 75-0589), and no other impurity phase appears. This indicates that the purity of the silicon powder was relatively high, and was consistent with the test results of energy dispersive X-ray spectroscopy (EDX) (Table 2). When the sample was heated to 1250 °C by the conventional method for the nitridation reaction, the XRD peak of the sample showed no significant change compared with the silicon powder raw material. This indicates that there was no obvious nitridation reaction of silicon powder. When the temperature was raised to 1350 °C, the XRD pattern of the sample had an obvious Si3N4 peak, but the peak intensity of the Si phase was the highest. The residual silicon is about 12.1% analyzed by XRD. This indicates that the conversion of nitridation reaction was relatively lower, to be only about 81.24%, even though Si3N4 was generated when the conventional heating was raised to 1350 °C. This may be affected by the diffusion of nitrogen. Besides, the conventional heating for the nitridation reaction was consistent with the results of TGA, which indicated that a vigorous nitridation reaction occurred at 1350 °C, and was substantially completed at 1450 °C. Moreover, it can be seen from Figure 4 that there are some peaks of Si3N4 phase due to the oxidation of some Si powder. When a small amount of SiO2 is mixed in the Si powder, the Si3N4O phase is easily formed during the nitridation process and the reaction equations are described below

\[
\begin{align*}
\text{SiO}_2(s) + 2\text{N}_2(g) + 3\text{Si}(s) &\rightarrow 2\text{Si}_3\text{N}_4(s) \\
\text{SiO}_2(s) + \text{Si}_3\text{N}_4(s) &\rightarrow 2\text{Si}_2\text{N}_2\text{O}(s)
\end{align*}
\]

In addition, the samples of the nitridation reaction heated by microwaves were analyzed. The temperature of the nitridation reaction was set to 1250 °C, and the microwave power was 2000 W. The nitrogen pressure and the holding time were the same as traditional heating. It can be seen from Figure 4 that when the temperature was raised to 1250 °C by microwave heating, the silicon powder was almost completely nitridated. The XRD pattern of the sample corresponded to the β-Si3N4 peak, and a small amount of α-Si3N4 phase and traces of the residual Si phase were observed. The mass percentage of β-Si3N4, α-Si3N4, Si3N4O, and Si phases was analyzed to be 93.2, 4.7, 0.7, and 1.4%, respectively. The sample was mainly of the β-Si3N4 phase after the nitridation reaction. Moreover, the conversion of nitridation reaction can reach 97.69%. This indicates that the nitridation reaction can be completed at a lower temperature and within a shorter time by microwave heating, which has the advantages of rapid reaction rate and high efficiency.

The energy consumption of the nitridation process by conventional heating and microwave irradiation was calculated. The energy consumption during the heating process and the reaction process (holding stage) was calculated. The results are shown in Table 1. From the table, we can see that with a microwave power of 2000 W (the conversion rate of electrical energy to microwave energy is generally 0.7–0.8), the energy required for heating to 1250 °C in 30 min and holding for 20 min is about 1.8 kW·h. When using conventional heating, the
energy required for heating to 1250 °C at a heating rate of 10 °C/min and holding for 20 min is about 15.8 kW·h, and the energy required for heating to 1350 °C is about 17.7 kW·h. The energy consumption of the microwave heating process is much lower than that of the conventional heating.

Figure 5 presents scanning electron microscopy (SEM) images of the raw material and silicon nitride samples. Figure 5a shows the raw material of silicon powder, and its morphology is mainly silicon scrap. Figure 5b,c shows the nitridation products by conventional heating at 1250 and 1350 °C, respectively. Figure 5d shows the nitridation product by microwave heating at 1250 °C. It can be seen from Figure 5d that when the powder is heated to 1250 °C by conventional heating, there is no significant change in the shape of silica powder. The result indicates that the reaction temperature was not reached, and no obvious nitridation reaction occurred, which is consistent with the XRD analysis. When the temperature reached 1350 °C, the morphology of the sample changed, and larger silicon nitride crystals were formed. However, there was still a large amount of residual silicon powder without nitridation. This indicates that although a part of the silicon powder had been nitridated, the conversion rate of the reaction was lower. Furthermore, it can be seen from Figure 5d that the morphology of the crumb-like silicon powder completely crystallized into larger-sized particles at 1250 °C, and the size and the shape are relatively uniform and mainly columnar. The result indicates that the nitridation reaction by microwave heating was more efficient than traditional heating. The nitridation temperature can be reduced by more than 100 °C by microwave heating, and the morphology of the reaction products was more uniform.

2.5. Effect of the Reaction Time on the Nitridation Process. Figure 6 illustrates the XRD patterns of samples after different reaction times. The power of the microwave was set to 2000 W, and the reaction temperatures were set to 1250 °C for the holding times of 5, 10, and 20 min. The N2 pressure was maintained at 121 kPa. It can be seen from the XRD patterns that there are silicon phase, β-Si3N4 phase, α-Si3N4 phase, and Si2N2O phase in the sample when it is held at 1250 °C for only 5 min. This indicates that the nitridation reaction of silicon powder was incomplete (the conversion is only 83.93%), and there were more residual silicon and intermediate phases. When the holding time was 10 min, the XRD peak of the sample corresponded well with β-Si3N4. The amounts of the residual silicon phase and the α-Si3N4 phase were small. The conversion of the nitridation reaction reached 97.03%, indicating that the silicon powder had been basically nitridated 10 min after the reaction. When the holding time was extended to 20 min, the diffraction intensity of the silicon phase and the α-Si3N4 phase was further reduced or disappeared. The product was mainly β-Si3N4, and only a small amount of α-Si3N4 phase and silicon phase remained. The nitridation reaction was completed with a conversion of 97.69%. The conversion of nitridation reaction after different reaction times is shown in Figure 7. The results indicate that the conversion of the nitridation reaction increases with time, but the reaction is almost complete after 10 min. Thus, the direct nitridation reaction by microwave heating of silicon powder could achieve good results within 10–20 min. Compared with other traditional processes, which usually Table 1. Energy Consumption of Microwave Nitridation and Conventional Nitridation

|                      | average current/(A) | average voltage/(V) | energy consumption/(kW·h) | total energy consumption/(kW·h) |
|----------------------|---------------------|---------------------|---------------------------|-------------------------------|
| microwave            |                     |                     |                           |                               |
| heat up to 1250 °C, 30 min | 7.4                | 380                 | 1.4                       | 1.8                           |
| holding 20 min       |                     |                     |                           |                               |
| conventional         |                     |                     |                           |                               |
| heat up to 1250 °C, 10 °C/min | 18.2               | 380                 | 14.4                      | 15.8                          |
| holding 20 min       |                     |                     | 1.4                       |                               |
| conventional         |                     |                     |                           |                               |
| heat up to 1350 °C, 10 °C/min | 18.9               | 380                 | 16.2                      | 17.7                          |
| holding 20 min       |                     |                     | 1.5                       |                               |

Figure 5. SEM images of the sample under different conditions: (a) raw materials, (b) conventional heating at 1250 °C, (c) conventional heating at 1350 °C, and (d) microwave heating at 1250 °C.

Figure 6. XRD patterns of samples after different reaction times.
take 1−5 h or longer, this method significantly shortens the process of the nitridation reaction of silicon powder.\textsuperscript{13,14,26,27}

Figure 8 shows the SEM images of samples at different holding times. In Figure 8a, the morphology of the sample is complex, with filamentous, granular, and flocculent crystals at the temperature of 1250 °C for 5 min. This indicates that the nitridation reaction is insufficient. When the temperature was maintained for 10 min, the morphology of the sample was relatively uniform, and mainly composed of columnar crystals. However, the surface was flocculent and relatively rough, and there were still a small number of filaments. When the temperature was maintained for 20 min, the morphology of the sample was relatively uniform, mainly composed of columnar crystals, and no filaments were observed. This indicates that the silicon powder had completed the nitridation reaction and formed a relatively uniform phase when the temperature was held for 20 min. The SEM microstructures were consistent with the phase analysis based on XRD.

2.6. Effect of N$_2$ Pressure on the Nitridation Process.

In addition, the effect of different N$_2$ pressures on the nitridation reaction of silicon powder was investigated. Wang et al. reported the preparation of silicon nitride powder by combustion synthesis under a low N$_2$ pressure of 140−200 kPa. In this study, the microwave power was set to 2000 W, the temperature was raised to 1250 °C, and kept for 20 min. The N$_2$ pressure was set to 106, 111, and 121 kPa. Figure 9 illustrates the XRD patterns of samples under different N$_2$ pressure conditions. When the N$_2$ pressures were 106 and 111 kPa, the diffraction intensity of the silicon phase and of α-Si$_3$N$_4$ was higher, indicating that there were more silicon residues and α-Si$_3$N$_4$ formed by nitridation reactions, and the nitridation reaction was incomplete. In addition, more Si$_3$N$_2$O phases were formed, which may be due to oxidation. The conversions of nitridation reaction under the N$_2$ pressures of 106 and 111 kPa were only 84.33 and 89.24%, respectively. As the N$_2$ pressure increased to 121 kPa, the diffraction intensities of the silicon phase and the α-Si$_3$N$_4$ phase in the sample were significantly reduced. The silicon powder was almost nitridated to form β-Si$_3$N$_4$, and only minimal amounts of α-Si$_3$N$_4$ and silicon phases were left, which meant that the nitridation reaction was more thorough. The conversion of nitridation reaction increases with N$_2$ pressure, as shown in Figure 10. Therefore, this study indicates that under the conditions of rapid nitridation of silicon powder heated by microwaves, a suitable increase in the N$_2$ pressure is beneficial to the nitridation reaction of silicon powder. This may be due to the promotion of the diffusion of nitrogen atoms inside the silicon crystal under pressure, which accelerates the nitridation of silicon atoms. This result is consistent with the study of Atkinson et al.\textsuperscript{44}

![Figure 7](image1.png)

**Figure 7.** Conversion rate after different reaction times.

![Figure 8](image2.png)

**Figure 8.** SEM images of samples at different holding times: (a) 5, (b) 10, and (c) 20 min.

![Figure 9](image3.png)

**Figure 9.** XRD pattern of samples at different N$_2$ pressures.

![Figure 10](image4.png)

**Figure 10.** Conversion rate at different N$_2$ pressures.
Figure 11 illustrates the SEM images of samples under different N\textsubscript{2} pressure conditions. It can be seen from Figure 11 that when the N\textsubscript{2} pressure is 106 kPa, a large amount of silicon scrap is not nitridated, and the formed silicon nitride particles have a sheet shape. When the N\textsubscript{2} pressure is 111 kPa, there is little silicon scrap left, and the silicon nitride particles crystallize and grow. When the N\textsubscript{2} pressure is 121 kPa, the nitridation reaction is better; there is no residual silicon powder; and the uniform silicon nitride crystal is formed.

2.7. Mechanism of Nitridation Process. Conventional heating is a slow heating process from the outside to the inside, as shown in Figure 12a. The surface temperature of the sample is relatively high and uniform, so the nitridation reaction is preferentially performed and a uniform silicon nitride layer is formed, which will block the diffusion of nitrogen and cause some resistance to further nitridation. In addition, silicon nitride has good thermal insulation properties, which will hinder further reaction of the internal silicon, as shown in Figure 12c, so the nitridation reaction by traditional heating requires a higher temperature, and the conversion rate is lower. Microwave heating is achieved by in situ conversion of electromagnetic energy inside the material. However, it is difficult to measure it in the actual experiment because of the internal heating characteristics of microwaves. Therefore, we combined with the actual experiment the calculation and simulation of the distribution characteristics of the electromagnetic field and the related literature reports\textsuperscript{45−47} to explain the obtained results. Moreover, while some areas will rapidly heat, the adjacent areas will achieve rapid heating through heat transfer, as shown in Figure 12b; this greatly shortens the heat transfer distance, and hence microwave heating has a higher heating rate. Furthermore, the temperature around the hot spot is too high resulting in local overheating, and reaching the local nitridation reaction temperature. Thus, the nitridation reaction of Si may occur in advance at the hot spots, and the overall temperature of the material is not too high. This will not form a completely wrapped silicon nitride layer, so the diffusion of nitrogen and further reaction will not be hindered (as Figure 12d). In addition, microwaves can penetrate the silicon nitride layer on the silicon surface and continue to heat the inner part. Therefore, microwave heating can reduce the temperature of the silicon powder nitridation reaction and improve the conversion efficiency of the nitridation reaction.

Figure 11. SEM image of samples at different N\textsubscript{2} pressures: (a) 106, (b) 111, and (c) 121 kPa.

Figure 12. Nitridation mechanisms heated by conventional heating and microwave irradiation: (a,c) conventional process; (b,d) microwave process.
3. CONCLUSIONS

In order to realize the preparation of silicon nitride from the industrial waste silicon powder by direct nitridation, the microwave heating–nitridation technology was applied in this study. Microwave heating of silicon powder has a higher heating rate, which significantly shortened the nitridation reaction time, improved the preparation efficiency of silicon nitride powder, and also greatly reduced the energy consumption. Compared with traditional heating, microwave heating can reduce the nitridation temperature of silicon powder by more than 100 °C. The conversion of the nitridation reaction is over 97%, and the obtained sample is mainly β-Si₃N₄. Moreover, with the increase of the reaction time and nitrogen pressure, the nitridation effect is better. When the nitridation reaction of silicon powder by microwave heating was conducted at 1250 °C for 20 min under the pressure of 121 kPa, excellent results were obtained in this study. The obtained product was mainly β-Si₃N₄ and its morphology was uniform and columnar.

4. EXPERIMENTAL SECTION

4.1. Materials and Processes. The solar-grade waste polysilicon powder was provided by RZL (ReneSola Zhejiang Ltd.), which was produced during the cutting process of polysilicon chips. The purity of silicon powder was more than 99.9%, which was determined using a Shimadzu energy dispersive X-ray fluorescence analyzer. The composition and the content of raw materials are shown in Table 2. The average particle size of the silicon powder was around 74 μm, measured using a laser particle size distribution analyzer (HYL-1076). N₂ used in the experiment was industrially pure. The silicon powder was placed in a corundum crucible; the corundum crucible, filled with nitrogen. The process was repeated three times, and the nitrogen gas was then continuously injected into the furnace chamber to ensure that the pressure was maintained at 100–125 kPa. The sample was heated by the microwaves at a frequency of 2.45 GHz. The schematic of microwave nitridation is presented in Figure 13. To study the influence of microwaves on the heating characteristics of silicon powder, the power of the microwave oven was set to 1500, 2000, and 2500 W. When the temperature rose to the set temperature (1150, 1250 and 1350 °C), it was kept for 5–20 min. The nitridation reaction equation is given below

$$3\text{Si}(s) + 2\text{N}_2(g) \xrightarrow{1100–1500 \degree C} \text{Si}_3\text{N}_4(s)$$  (3)

Table 2. Composition and Content of Si Powder Raw Materials (wt %)

| composition | Si  | Ni  | Fe  |
|-------------|-----|-----|-----|
| content     | 99.974 | 0.020 | 0.006 |

After cooling to room temperature, the samples were taken out for analysis. During the experiment, an infrared thermometer was used to measure the temperature.

4.2. Characterization Method. TGA data were collected using a TG and DTG analyzer (STA 449 F3 Jupiter, Netzsch, Germany). The starting material (3.083 mg) was heated from 25 to 1500 °C at 10 °C/min under an N₂ atmosphere (20 mL/min), and another starting material (3.543 mg) was heated from 25 to 1200 °C at the rate of 10 °C/min under an oxygen atmosphere (20 mL/min). The temperature raising dielectric properties of samples were measured by cavity perturbation method. The process of measuring the dielectric properties by the cavity perturbation method has been described in our previous research. The temperature range of the raw material test was from room temperature to 1000 °C. The microscopic morphology and microstructure of samples were observed using a scanning electron microscope (TESCAN VEGA3 SBH, Czech). The phase transition of silicon powder during the nitridation process was analyzed by XRD (PANalytical X'Pert3 Powder, the Netherlands), and XRD patterns were obtained using CuKα radiation (λ = 1.54060 Å) at 40 kV, 40 mA, and a scan rate of 8°/min. The relative amounts of various phases in the samples were determined according to the method reported by Gazzara and Messier. The conversion rate of Si is expressed as follows

$$P = \frac{W_{S1}}{W_{S0} + W_{S1}} \times 100\%$$  (4)

where P is the conversion rate; W_{S0} is the content of free Si; and W_{S1} is the content of compound Si.

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