New technique to synthesize silicon nitride nanopowder by discharge-assisted reaction of silane and ammonia

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Abstract
In this work, the chemical reaction of silane and ammonia gases was induced and assisted by electric power transferred to the reaction volume throughout argon discharge at pressures of about 3 mbar. This power was applied to the reaction volume as short pulses with different durations to produce highly-pure polycrystalline Si₃N₄ nanoparticles. The number of crystal planes was decreased by using shorter pulses of discharge power. The minimum nanoparticle size was 26.10 nm for the sample prepared using discharge pulse duration of 0.1 ms. This is the first attempt to employ fast discharge pulses to induce and assist the chemical reaction of silane and ammonia to produce highly-pure silicon nitride nanopowders.

1. Introduction
A prime driver for the development silicon nitride was to replace metals with ceramics in advanced turbine and reciprocating engines for higher operating temperatures and efficiencies [1, 2]. Among all nitride compounds, it has been widely used because of its transparency, hardness, impermeability, and other advantageous functional properties [3, 4]. Silicon nitride is unreplaceable material in some applications such as silicon-on-insulator (SOI) electronics [5, 6], high-temperature standing materials [7], hard optical and photovoltaic material [8, 9], atomic force microscope (AFM) cantilevers [5], photonic crystals and nanocavities [10, 11], nanocomposites [2], and ultra-high vacuum (UHV) force sensors [5].

Silicon nitride nanostructures are synthesized and prepared by various methods and techniques of physical vapor deposition (PVD) and chemical vapor deposition (CVD) [12–27]. The normal reaction of silane (SiH₄) and ammonia (NH₃) leads to the formation of silicon nitride (Si₃N₄) as follows [28]:

\[
3\text{SiH}_4 + 4\text{NH}_3 \xrightarrow{\Delta} \text{Si}_3\text{N}_4 + 24\text{H}_2
\]  

At high pressures of the reacting gases, the metallic discharge electrodes may act as a catalyst especially at high temperature of plasma column and cause to prevent a fraction of the nitrogen atoms resulted from the decomposition of NH₃ molecules to bond to silicon atoms resulted from the decomposition of SiH₄ molecules. Hence, silicon may appear in its free form in the final product as

\[
6\text{SiH}_4 + 8\text{NH}_3 \xrightarrow{\Delta} 3\text{Si(s)} + \text{Si}_3\text{N}_4(s) + 4\text{NH}_3(g) + 18\text{H}_2(g)
\]  

The chemical structure of silicon nitride gives this compound its featured properties when compared to similar compounds [29].

The final product of this reaction can be varied by controlling the molar concentrations of starting materials as well as providing high power as short pulses to the reactants [30]. Electrons in the plasma cause dissociation of source gases into a reactive species that both react in the gas phase and produce precursor molecules [28].

In this work, Si₃N₄ nanoparticles are synthesized by a new technique to induce and assist the chemical reaction of SiH₄ and NH₃ gases at pressures of about 3 mbar. The proposed technique may provide some advantages over the available techniques, such as higher quality of prepared nanostructures, lower production cost, and lower experimental difficulty.
2. Experimental work

Deposition chamber is first evacuated down to $10^{-5}$ mbar using Leybold–Heraeus rotary pump of 9 m$^3$ hr$^{-1}$ suction power and Leybold diffusion pump of 3600 m$^3$ hr$^{-1}$ suction power to remove any residuals or contaminants. Argon gas at pressure of 0.5 mbar was used to generate the glow discharge between two electrodes made of titanium. Titanium was used for electrodes in order to minimize contamination from electrode materials in the final product. Highly-pure (0.99) silane (SiH$_4$) and ammonia (NH$_3$) were used as precursors to produce silicon nitride and the final pressure of SiH$_4$–NH$_3$ gas mixture reaches to 3 mbar. A magnetron was maintained at the cathode in order to accelerate the electrons generated by the electric discharge of argon to cross the volume between the electrodes and hence hit the SiH$_4$ and NH$_3$ molecules existing in between. This causes the decomposition of these molecules and hence induces the chemical reaction leading to form silicon nitride molecules. Argon was chosen due to its low breakdown voltage ($\sim$190 V at 35 mA) compared to SiH$_4$ and NH$_3$, therefore, small amount ($\sim$0.033%) of the minimum applied power is consumed for the generation of plasma column to represent the resistor through which the remaining power ($\sim$99.96%) is transferred to the reaction volume to induce the reaction between SiH$_4$ and NH$_3$. The discharge power from a homemade power supply (5–6 kV, 4–5 A) is applied between the electrodes as pulses of different durations. A pulse forming network (PFN) was used to convert the DC signal of the power supply into short pulses. A wide range of pulse duration (10 $\mu$s to 50 ms) was employed but the results of three values only were reported herein (0.1, 0.5 and 1 ms) as the optimum. The pulse repetition rate of the discharge could be precisely varied in the range 1 Hz to 1 kHz. Figure 1.
shows schematically the experimental system used in this work and figure 2 shows the equivalent circuit of reference divider and the variation of percent difference of peak voltage with pulse duration. The proposed design of discharge assembly mainly exhibit some advantages such as formation of homogeneous discharge cross section, avoidance of sharp discharge regions and corners at which the electric field intensity is maximized, minimization of the straight reflection of gas molecules and hence maximization of the number of molecules within discharge volume, and generation of two discharge regions that would highly ensure the continuous motion of ions from side to side under the effect of magnetron.

The structural characteristics of prepared samples were determined by a Bruker, 1.54.5 Å CuKα radiation x-ray diffractometer (XRD), Shimadzu FTIR-8400S Fourier-transform infrared (FTIR) spectrometer, TESCAN Vega EasyProbe scanning electron microscope (SEM), and Agilent 5977B gas chromatography-mass spectrometry (GC-MS) instrument.

3. Results and discussion

Figure 3 shows the XRD patterns of the synthesized silicon nitride samples using glow discharge pulses of different durations. The sample synthesized using glow discharge pulse of 0.1 ms shows two peaks belonging to
silicon in its radical form; the first is apparent and high at \(2\theta = 28.30^\circ\) and the second is at \(47.15^\circ\). Also, four distinct peaks of polycrystalline silicon nitride are observed [31].

The sample prepared using 0.5 ms discharge pulse duration shows peaks corresponding to the crystal planes of (232), (110), (200) and (101) with reasonable decrease in the first peak of unbounded silicon (28.30°), as shown in figure 3. Using discharge pulse duration of 1 ms resulted in appearance of two new peaks belonging to silicon nitride corresponding to the crystal planes of (321) and (301) in addition to the peaks observed in the middle pattern in figure 3 and the unbounded silicon still exist in the final product, as shown in the lower pattern in figure 3.
These results can be ascribed to the effect of pulse duration to provide the power required by the chemical reaction to occur leading to form silicon nitride and the fact that some crystal planes do not find enough time to grow at shorter pulse durations, while some other planes, such as (110), (200), (321) and (101), are immediately formed. Short pulse duration is clearly enough to decompose SiH₄ and NH₃ molecules but not enough to bond all silicon atoms to nitrogen atoms and form silicon nitride molecules. Using longer pulse duration caused to provide longer time for more Si atoms to bond to N while smaller amount of them did not. Beside, more silicon nitride with new crystal orientations was formed. The PFN used in this work could not produce pulse duration longer than 1 ms.

Figure 4 shows the FTIR spectrum of the silicon nitride sample synthesized by applying discharge pulse duration of 0.1 ms. The broad band around 950–1100 cm⁻¹ is attributed to the stretching mode of Si–N bond [32]. However, the peak at 1405 cm⁻¹ is a characteristic for the sp³-bonded Si–N [33]. The peak around 1519 cm⁻¹ is ascribed to the stretching mode of double Si=N bond [34]. The peak around 1652 cm⁻¹ is also attributed to the stretching vibration of Si–N bond [32]. These peaks can be overlapped with other peaks within 1000–1800 cm⁻¹ ascribed to the bonded silicon layers, which become active in the infrared region as their symmetry is broken due to the incorporation of nitrogen atoms in these layers [22]. The peaks observed below 950 cm⁻¹ are attributed to the Si–H bond [15, 34]. Other peaks observed around 2900 and 3340 cm⁻¹ are attributed to the SiHₓ and NHₓ groups, respectively, as precursors of silicon nitride molecules [35]. The peaks observed during 2600–2000 cm⁻¹ are attributed to NH⁺ stretching and vibration modes of charged amines and their derivatives. Also, the stretching mode of Si–H bond lies within the same region of wavenumbers. The peaks observed during 3900–3700 cm⁻¹ are attributed to the single bond absorption of hydrogen with some other elements, e.g., O–H, N–H, C–H, etc [32, 33].

Figure 5 shows the results of SEM for the samples synthesized using five different pulse durations (0.1, 0.25, 0.5, 1 and 2 ms). It is clear that using shorter discharge pulse duration results in smaller particles (figure 5(a)) with minimum particle size of 26.10 nm and the particle size gets larger when longer pulse durations are used (figures 5(b) and (c)) with minimum particle size of 34.55 and 40.05 nm, respectively. Furthermore, the aggregation within the formed nanostructures is observed at some locations in figure 5(b) while it dominates the structure in figure 5(c). This is attributed to the time available for the crystallites to form larger nanoparticles and hence aggregate as the crystal growth is limited to the crystal planes appeared in the XRD patterns. Accordingly, compromise is required to produce as much as possible of silicon nitride molecules with nanostructures free of aggregation. Figure 6 shows the variation of minimum nanoparticle size determined from SEM with discharge pulse duration for five different values (0.1, 0.25, 0.5, 1 and 2 ms). It is clear that the minimum particle size is increased as the discharge pulse gets longer since the time allowed for the small silicon nitride particles to grow further. As the discharge pulse duration was increased from 0.1 to 1 ms, the percentage increase in the minimum nanoparticle size was about 15%, whereas it drastically increased by more than 150% as the discharge pulse
duration was further increased to be 2 ms. This is an indirect indication for the formation of larger particles and hence aggregation, as shown in figure 5(d).

The result of energy-dispersive x-ray spectroscopy (EDX) shown in figure 7 is for the sample synthesized with pulse duration of 0.1 ms. This result confirms the structural purity of this sample as only peaks belonging to silicon and nitrogen are seen with 42.85 and 57.14%, respectively.

Figure 8 shows the results of gas chromatography and mass spectroscopy (GC-MS) for the sample synthesized with pulse duration of 0.1 ms. In this figure, the most intensive peak is observed at retention time of 17822 ms, whose mass spectrum is shown in the inset figure. Relatively high peaks are assigned to the silicon nitride, its precursors and byproducts, shown in equation (2), mainly silicon and ammonia. As well, no accountable traces belonging to other elements or compounds were observed.
Figure 6. Variation of minimum nanoparticle size with discharge pulse duration.

Figure 7. The EDX result for the sample prepared using discharge pulse duration of 0.1 ms.

Figure 8. GC spectrum (main) and MS analysis (inset) of the sample prepared using discharge pulse duration of 0.1 ms.
4. Conclusion

In concluding remarks, the chemical reaction of SiH$_4$ and NH$_3$ gases can be controlled towards the production of Si$_3$N$_4$ nanoparticles. This control is performed by applying high discharge power as short pulses to the reaction volume. The pulse duration was found very important to control the number of grown crystal planes, nanoparticle size and aggregation in the prepared nanostructures. The synthesized silicon nitride nanoparticles were polycrystalline with the presence of unbounded Si atoms in the final product and these nanoparticles can be considered as highly-pure nanostructures. The minimum nanoparticle size was 26.10 nm for the sample prepared using discharge pulse duration of 0.1 ms. The technique proposed in this work is new, reliable and low-cost to synthesize compound nanoparticles and functional nanomaterials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflicts of interest/Competing interests

The author declares that he does not have any conflict of interest related to this work.

Code availability (software application or custom code)

Not applicable.

Author contributions

The author has designed, constructed and operated the system used in this work. He also has collected and analyzed the results, and finally written the manuscript.

Compliance with ethical standards

The author declares that this work was prepared to comply with ethical standards and there is no potential conflicts of interest. As well, author declares that the research does not involve Human Participants and/or Animals. He did not need for any informed consent related to publication of his work.

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