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Highly-Pure Silicon Nitride Nanomaterial Prepared by Chemical Nitridation Method

In this work, highly-pure silicon nitride nanopowders were prepared by chemical nitridation method. The tetraethyl orthosilicate (TEOS) was used as a precursor for silicon alkoxide while ammonia was used as a precursor for nitrogen. The structural characteristics of the prepared nanopowders were determined and studied as functions of annealing temperature carried out during the preparation method. The chemical method used in this work can be characterized by low cost, simple requirements, and reliability to produce highly-pure nanopowders. Results showed that the prepared nanopowders largely maintain an amorphous or highly nanocrystalline structure, even at 1100 °C. Significant crystallization into well-defined crystalline phases of Si_3N_4 does not occur under these annealing conditions. While the material remains nanostructured, annealing at higher temperatures (especially 1100 °C) leads to some degree of particle growth or rearrangement, even without full crystallization. The silicon (Si) and nitrogen (N) peak intensities remain largely consistent, indicating that the stoichiometry of Si_3N_4 is maintained. A small carbon is residual from the chemical nitridation process or atmospheric contamination. This impurity appears to be stable or present consistently across the different annealing temperatures. The chemical nitridation method, combined with annealing up to 1100 °C, primarily yields amorphous or highly nanocrystalline Si_3N_4 nanopowders. While higher temperatures promote some particle growth, they do not induce significant crystallization, and the overall elemental composition remains consistent with a minor carbon impurity.

Keywords: Silicon nitride; Chemical nitridation; Nanopowders; Nanostructures
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1. Introduction

Ceramic nanomaterials have attracted significant attention in scientific and industrial research due to their numerous advantages in meeting specific requirements that traditional, larger-scale ceramic materials cannot fulfill. Among the ceramic materials that have gained increasing interest since their discovery in the early 1900's is silicon nitride (Si_3N_4), a distinguished and rare ceramic material that contains neither oxygen nor carbon in its chemical composition, granting it high resistance to corrosion and oxidation at elevated temperatures [1-4]. Additionally, the metallic component in its structure is not a metal. The mechanical properties – particularly its lightweight nature, toughness, and extremely high hardness, surpassing many steel alloys and traditional ceramics – along with its thermal properties, such as high thermal stability (up to 1000°C) and low thermal conductivity, are key factors that make this material highly valuable in industry and technology [5,6]. Moreover, this material exhibits excellent surface properties and high reactivity, giving it a strong adsorption characteristics, which facilitated its growing use in agricultural, environmental, and biomedical applications, including water filtration, chemical reaction catalysis, and soil fertility enhancement [7,8]. It also shows excellent ability for surface modification, enhancing its chemical and biological interactions [9].

In recent years, too many studies have explored the spectroscopic and optical properties of silicon nitride nanomaterial and its applications in spectroscopy, optoelectronic devices, such as optical sensors, detectors, anti-reflective coatings in the visible and infrared regions of the electromagnetic spectrum (due to its tunable refractive index), as well as in LED manufacturing and in electro-optics as insulating or light-diffusing layers [10-12].

Production of silicon nitride nanomaterial presents challenges in controlling its properties to meet specific application requirements due to high costs and the complexity of manufacturing processes [13,14]. In chemical methods, the standard chemical reaction leading to form silicon nitride typically requires high temperatures (up to 1400°C) at atmospheric pressure [15]. Physical methods are usually conducted under vacuum to reduce the required formation temperature and prevent atmospheric components (e.g., oxygen, carbon dioxide, and water vapor) from reaching and contaminating the synthesized nanomaterial [16-18]. Combining chemical and physical methods for preparing silicon nitride nanomaterial can leverage the advantages of both methods to produce nanomaterials with unique and superior properties. For example, a chemical reaction between silicon and nitrogen sources can be conducted in a sealed, clean environment (e.g., vacuum chamber), can be energetically activated using plasma, electromagnetic radiation (e.g., laser), or electric and magnetic fields [19]. Additional physical methods, such as thermal annealing and ultrasonic waves, can be employed to enhance the quality of the material during synthesis [20,21].

Chemical nitridation is a thermochemical process that introduces nitrogen into the surface of a material, typically to form hard nitride compounds. This method can be achieved through various techniques like gas nitridation (using ammonia), liquid nitridation (using salt baths), or plasma nitridation [21,22]. Chemical nitridation generally occurs at lower temperatures than other hardening treatments, minimizing distortion and dimensional changes in the treated components. It can also improve corrosion resistance and reduce friction. The process can be time-consuming, especially gas nitridation which can take many hours [23,24]. Material selection is limited, as not all metals are suitable for nitridation. The depth of the nitrided layer is typically thin. Some methods, like traditional liquid nitriding, involve toxic cyanide salts, posing environmental and health concerns. High initial equipment costs can also be a barrier for plasma nitriding [25,26].

In this research, a multi-stage nitridation reaction under vacuum was used to prepare silicon nitride as a high-purity nanopowder. The structural and spectral properties of the synthesized material were then studied at different annealing temperatures.

2. Experimental Part

Tetraethyl orthosilicate ($Si(OC_2H_5)_4$ or TEOS) was used as a precursor for silicon alkoxide ($Si(OH)_4$) while ammonia (NH_3) was used as a precursor for nitrogen. Ethanol (C_2H_5OH) was used as an organic solvent, hydrochloric acid (HCl) was used to catalyze the chemical reaction, and citric acid ($C_6H_8O_7$) was used as a reduction agent.

Silica solution was prepared by dissolving 2 mg of silica in 5 mL of 10% concentrated ethanol with continuous stirring until the complete dissolving is achieved. A 100 µL of HCl acid was slowly added to the solution to induce the hydrolysis reaction to start as

$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH$

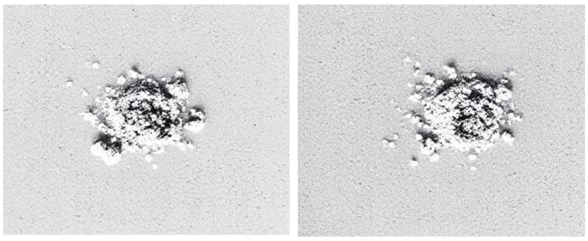
The solution is left on the stirrer for 5 min, then removed and left static to allow the initial formation of the gel, which depends on both pH and temperature of the solution.

After the solution is completely transformed into gel, the nitrogen-rich compound (NH_3) is added to the silica gel to start the nitridation reaction with slow and continuous stirring for 30 min. After that, the mixture of gel and ammonia is dried at 100 °C under vacuum (0.01 mbar) to remove the residual solvent and form the xerogel. Then the calcination process is carried out on the dried material at 600 °C in atmosphere to remove the organic residuals completely. The sample is then transferred to the tube furnace to perform the high thermal treatment (annealing) and nitridation throughout the slow heating of the dried gel in existence of ammonia up to certain temperature (200, 500, 800, or 1100 °C) for 4 hours to form silicon nitride as a result of the following reaction:

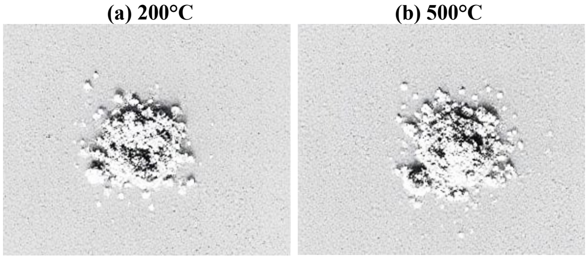
$3SiO_2 + 4NH_3 \rightarrow Si_3N_4 + 6H_2O$

The tube furnace is then slowly opened to allow the water vapor and ammonia to exit and a mixture of argon and nitrogen gases is pumped into the tube to perform thermal annealing at 800 °C to enhance the crystallinity of the annealed material. If aggregation is observed within the sample, it is sonicated at 100 MHz for 30 min to obtain nanoparticles with minimum size. Figure (1) shows the nanopowder samples prepared in this work.

The structural, morphological and spectroscopic characteristics of the prepared material were determined by x-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive x-ray spectroscopy (EDX), atomic force microscopy (AFM), Fourier-transform infrared (FTIR) spectroscopy, and UV-visible spectrophotometry.



(a) 200°C (b) 500°C



(c) 800°C (d) 1100°C

Fig. (1) Silicon nitride nanopowder samples prepared and annealed at different temperatures

3. Results and Discussion

The XRD patterns in Fig. (2) for Si_3N_4 nanopowder samples prepared by chemical nitridation and annealed at temperatures of 200, 500, 800, and 1100 °C, consistently display broad, diffuse peaks. This characteristic indicates that the materials are predominantly amorphous or possess a highly nanocrystalline structure across all tested temperatures. There is no clear evidence of distinct, sharp diffraction peaks that would signify the formation of well-ordered crystalline phases of Si_3N_4. As the annealing temperature increases, while some minor shifts or changes in peak intensity might be discernible upon closer inspection, the overall amorphous nature of the Si_3N_4 nanopowders persists, even at the highest annealing temperature of 1100 °C. This suggests that these annealing conditions are insufficient to induce substantial long-range atomic ordering and crystallization in the synthesized Si_3N_4 nanopowders [27].

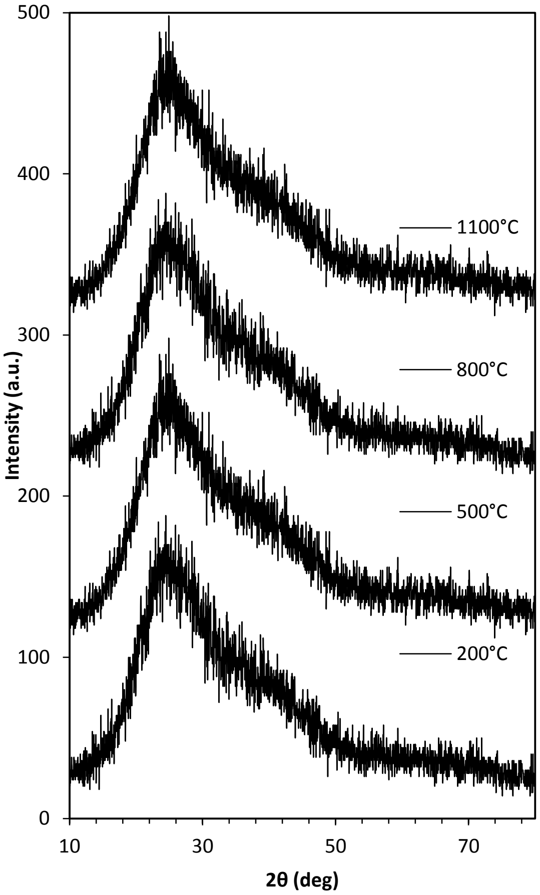
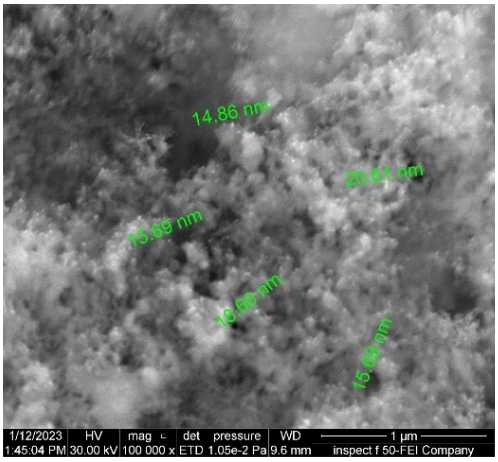
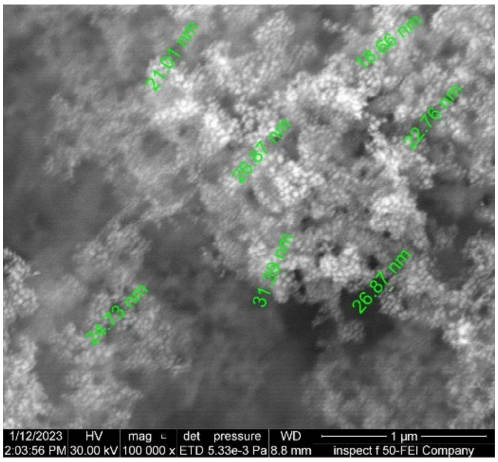


Fig. (2) XRD patterns of the silicon nitride nanopowders prepared and annealed at different temperatures

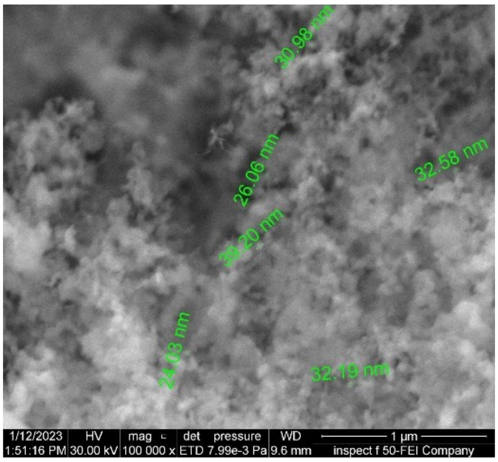
Figure (3) shows the FE-SEM images, which illustrate the morphological evolution of Si_3N_4 nanopowder samples prepared in this work with increasing annealing temperature. At 200°C (Fig. 3a), the material appears to consist of very fine, irregularly shaped nanoparticles, possibly with some degree of agglomeration. The individual particles are difficult to distinguish clearly, suggesting a highly disordered or amorphous structure, consistent with the XRD findings. The particle size is ranging within 14-20 nm. As the temperature increases to 500°C (Fig. 3b) and 800°C (Fig. 3c), there was a subtle but noticeable change. The images still show agglomerates of nanoparticles, but there might be a slight increase in the average particle size, and some individual particles appear a bit more defined, although still largely irregular. The overall morphology remains consistent with a nanostructured, possibly amorphous or nanocrystalline, material. The particles size showed an increase up to 18-32 nm and 24-40 nm, respectively. At 1100°C (Fig. 3d), the particles appear to be larger and more distinct compared to the lower temperatures. While significant crystal growth or well-defined facets are not evident, there was a clear trend towards increased particle size (27-36 nm) and a reduction in the most finely dispersed, highly amorphous-looking regions seen at lower temperatures. This suggests that higher temperatures facilitate some degree of particle growth and potentially minor densification or rearrangement, even if full crystallization is not achieved, as indicated by the XRD patterns. The images collectively show that annealing at higher temperatures leads to larger, more discernible particles, though the material largely retains its nanostructured character.



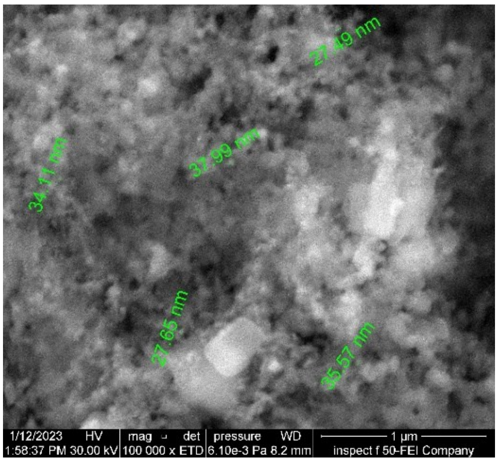
(a) 200°C



(b) 500°C



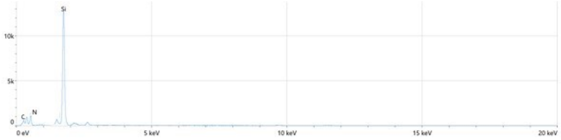
(c) 800°C



(d) 1100°C

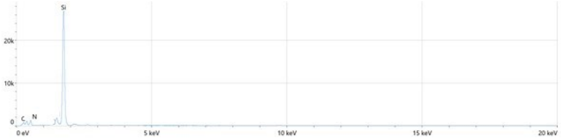
Fig. (3) FE-SEM images of the silicon nitride nanopowders prepared and annealed at different temperatures

The EDX spectra shown in Fig. (4) for Si_3N_4 nanopowder samples, annealed at 200, 500, 800, and 1100 °C, consistently indicate prominent peaks corresponding to silicon (Si) and nitrogen (N). This confirms the primary elemental composition of the synthesized material as Si_3N_4. Additionally, a small carbon (C) peak is observable in all spectra, likely originating from residual carbon from the chemical nitridation process or atmospheric contamination.



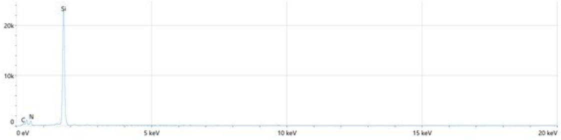
Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	25.5	0.9	18.0	0.6
N	40.4	0.8	34.5	0.7
Si	34.1	0.1	46.4	0.1

(a) 200°C



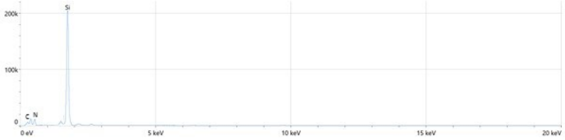
Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	27.4	0.8	18.4	0.5
N	35.5	0.5	30.2	0.4
Si	37.1	0.1	51.6	0.2

(b) 500°C



Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	21.6	0.7	14.4	0.4
N	40.8	0.7	33.5	0.5
Si	37.6	0.1	52.2	0.2

(c) 800°C



Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	23.2	0.3	15.9	0.2
N	42.7	0.2	36.6	0.2
Si	34.1	0.1	47.4	0.1

(d) 1100°C

Fig. (4) EDX results of the silicon nitride nanopowders prepared and annealed at different temperatures

Comparing the spectra across different annealing temperatures, the relative intensities of the Si and N peaks appear to remain largely consistent, suggesting that the stoichiometric ratio of Si to N in the nanopowders is maintained throughout the annealing process. There are no significant new peaks appearing or disappearing, nor are there drastic changes in the Si/N ratio that would indicate major phase transformations or significant impurity incorporation at higher temperatures. The presence of the carbon peak, while minor, also seems to persist across all temperatures, indicating its stability or continued presence within the samples.

Conclusion

In concluding remarks, the prepared nanopowders largely maintain an amorphous or highly nanocrystalline structure, even at 1100 °C. Significant crystallization into well-defined crystalline phases of Si_3N_4 does not occur under these annealing conditions. While the material remains nanostructured, annealing at higher temperatures (especially 1100 °C) leads to some degree of particle growth or rearrangement, even without full crystallization. The silicon (Si) and nitrogen (N) peak intensities remain largely consistent, indicating that the stoichiometry of Si_3N_4 is maintained. A small carbon is residual from the chemical nitridation process or atmospheric contamination. This impurity appears to be stable or present consistently across the different annealing temperatures. The chemical nitridation method, combined with annealing up to 1100 °C, primarily yields amorphous or highly nanocrystalline Si_3N_4 nanopowders. While higher temperatures promote some particle growth, they do not induce significant crystallization, and the overall elemental composition remains consistent with a minor carbon impurity.

References

[1] N. Maluf and K. Williams, **"An Introduction to Microelectromechanical Systems Engineering"**, Artech House, Inc. (2004), p. 19, 39.

[2] S.C. Danforth, W. Symons, K.J. Nilsen, R.E. Riman, in: J.G.P. Binner (Ed.), **"Advanced**

Ceramic Processing and Technology", Willian Andrew Publishing (Noyes, 1990), pp. 39–71.

[3] F.J. Kadhim, M.K. Khalaf and O.A. Hammadi, "Preparation and Characterization of Silicon Nitride Nanostructures Prepared by DC Reactive Sputtering Technique with Novel Design of Closed-Field Unbalanced Dual Magnetron Assembly", *Iraqi J. Appl. Phys.*, 13(3) (2017) 3-12.

[4] Yu.G. Dobrovolskiy, V.L. Perevertailo and B.G. Shabashkevich, "Anti-reflection coatings based on SnO_2, SiO_2, Si_3N_4 films for photodiodes operating in UV and visible spectral ranges", *Semicond. Phys., Quantum Electron. Optoelectron.*, 14(3) (2011) 298-301.

[5] B.K. Nasser and M.A. Hameed, "Structural Characteristics of Silicon Nitride Nanostructures Synthesized by DC Reactive Magnetron Sputtering", *Iraqi J. Appl. Phys.*, 15(4) (2019) 33-36.

[6] Wei-Tang Li, "Effect of sputtering-gas pressure on properties of silicon nitride films produced by helicon plasma sputtering", *Thin Solid Films*, 384 (2001) 46-52.

[7] F.J. Kadhim, O.A. Hammadi, and A.A. Anber, "Spectroscopic Study of Chromium-Doped Silicon Nitride Nanostructures Prepared by DC Reactive Magnetron Sputtering", *Iraqi J. Appl. Phys.*, 17(2) (2021) 11-14.

[8] G. Xu, "Optical investigation of silicon nitride thin films deposited by r.f. magnetron sputtering", *Thin Solid Films*, 425 (2003) 196-202.

[9] D.A. Taher and M.A. Hameed, "Spectroscopic Characteristics of Silicon Nitride Thin Films Prepared by DC Reactive Sputtering Using Silicon targets with Different Types of Conductivity", *Iraqi J. Appl. Phys.*, 19(4A) (2023) 73-76.

[10] M. Vila, D. Cáceres and C. Prieto, "Mechanical properties of sputtered silicon nitride thin films", *J. Appl. Phys.*, 94(12) (2003) 7868-7873.

[11] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, "Fabrication and Characterization of UV Photodetectors Based on Silicon Nitride Nanostructures Prepared by Magnetron Sputtering", *Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys.*, 230(1) (2016) 32-36.

[12] G. Sashikesh, M.S. Ford and T.P. Softley, "Ionization of Rydberg H2 molecules at doped silicon surfaces", *J. Chem. Phys.*, 138 (2013) 114308.

[13] B.K. Nasser and M.A. Hameed, "Narrow Emission Linewidth of Highly-Pure Silicon Nitride Nanoparticles in Different Dye Solutions as Random Gain Media", *Nonl. Opt. Quantum. Opt.*, 53(1-2) (2019) 99-105.

[14] S.A. Awan and R.D. Gould, "Conductivity and dielectric properties of silicon nitride thin films prepared by RF magnetron sputtering using nitrogen gas", *Thin Solid Films*, 423 (2003) 267-272.

[15] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, "Silicon Nitride Nanostructures Prepared by Reactive Sputtering Using Closed-Field Unbalanced Dual Magnetrons", *Proc. IMechE, Part L, J. Mater.: Design Appl.*, 231(5) (2017) 479-487.

[16] X. Zhang and C.P. Grigoropoulos, "Thermal conductivity and diffusivity of free-standing silicon nitride thin films", *Rev. Sci. Instrum.*, 66(2) (1995) 1115-1120.

[17] A. Batan, "Characterisation of the silicon nitride thin films deposited by plasma magnetron", *Surf. Interface Anal.*, 40 (2008) 754-757.

[18] O.A. Hammadi, "Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctional FreezingAssisted Ultrasonic Extraction Method", *Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys.*, 232(4), 135- 140 (2018).

[19] M.A. Hameed and Z.M. Jabbar, "Preparation and Characterization of Silicon Dioxide Nanostructures by DC Reactive Closed-Field Unbalanced Magnetron Sputtering", *Iraqi J. Appl. Phys.*, 12(4) (2016) 13-18.

[20] O.A. Hammadi, "Effects of Extraction Parameters on Particle Size of Titanium Dioxide Nanopowders Prepared by Physical Vapor Deposition Technique", *Plasmonics*, 15 (2020).

[21] B. Bhushan (Ed.), **"Springer Handbook of Nanotechnology"**, Springer (2004), p. 27, 151, 438.

[22] P.M. Martin, **"Handbook of Thin Film Deposition Techniques"**, Elsevier (2010), p. 4.

[23] T. Mang, K. Bobzin and T. Bartels, **"Industrial Tribology: Tribosystems, Friction, Wear and Surface Engineering, Lubrication"**, Weinheim (January 2011).

[24] Zh.Q. Yao, "Studies of the composition, tribology and wetting behavior of silicon nitride films formed by pulsed reactive closed-field unbalanced magnetron sputtering", *Nucl. Instrum. Meth. in Phys. Res.*, B242 (2006) 33-36.

[25] Ru Xia et al., "Surface modification of nano-sized silicon nitride with BA-MAA-AN tercopolymer", *J. Appl. Polym. Sci.*, 107 (2008) 562-570.

[26] O. Debieu, "Structural and optical characterization of pure Si-rich nitride thin films", *Nanoscale Res. Lett.*, 8 (2013) 31.

[27] JCPDS 1979, C 29-1133, Joint Committee on Powder Standards, International Center for Diffraction Data, USA (1979).