**Formation of Aligned α-Si3N4 Microfibers by Plasma Nitridation of Si (110) Substrate Coated with SiO2**

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Abstract: Plasma nitridation of an amorphous SiO2 layer on Si (110) substrate can form well-aligned α-Si3N4 crystallites in fibrous morphology. Nitriding is performed at a temperature in the range of 800–1000 °C by using microwave plasma with a gas mixture of N2 and H2. Raman spectroscopy shows the characteristics of an α-Si3N4 phase without other crystalline nitrides. As shown by scanning electron microscopy, the formed α-Si3N4 microfibers on the Si substrate can be in a dense and straight array nearly along with Si 〈110〉, and can have a length over 2 mm with a diameter in the range of 5–10 μm. Structural characterization of scanning transmission electron microscopy in cross section view reveals that the elongated α-Si3N4 crystallites are formed on the surface of the nitrided SiO2/Si (110) substrate without any interlayers between Si3N4 and Si, and the longitudinal direction of α-Si3N4 appears mainly along 〈1120〉, which is approximately parallel to Si 〈110〉.

Keywords: Si3N4; plasma; nitridation; fiber; electron microscopy

1. Introduction

Silicon nitride (Si3N4) has been used in many structural applications for a long time due to its excellent properties, such as high hardness and high-temperature stability, resistance to thermal shock, and wear resistance. In addition, Si3N4 has a wide band gap (EG = 4.7 eV) which can be applied for semiconductor devices [1,2]. Si3N4 has many different crystal structures, among which α-Si3N4, β-Si3N4, and γ-Si3N4 are common phases. Both α-Si3N4 and β-Si3N4 can be formed under ambient conditions at high temperatures, while γ-Si3N4 exists under high temperature and high pressure [3–5]. In addition, crystalline Si3N4 synthesis, generally in polycrystalline microstructure, has been widely conducted by nitridation of Si and SiO2 powders at high temperature. Plasma nitriding has been proven to be effective for material synthesis [6–8]. Plasma nitridation of SiO2 and Si for the formation of Si3N4 have been studied in previous reports by using thermal and radio frequency plasma processes with gases containing nitrogen [9–11] in which hydrogen may be necessary for the oxide reduction, and nitrogen reaction with Si formed nitride. It is well known that microwave plasma can easily achieve high plasma density which has been applied in various applications, including etching and film deposition. In our recent studies, we have shown that microwave plasma can be effectively applied for nitridation of c-plane and m-sapphires to form epitaxial AlN. In addition, epitaxial TiN can obtain plasma nitridation of rutile TiO2 [12–14]. Various forms of crystalline Si3N4 have been synthesized, including whiskers and nanowires which may have potential applications in nanocomposites and electronic devices. Si3N4 nanowires have been synthesized by various methods, including chemical vapor deposition and nitridation [15–18]. Recently, we have used microwave plasma for nitridation of a SiO2/Si (111) substrate to form [1010]-oriented crystalline α-Si3N4 and
β-Si$_3$N$_4$ which have elongated wire morphologies in lengths of several hundred micrometers and are mainly aligned with three different Si <110> directions [19]. In this study, the formation of crystalline Si$_3$N$_4$ on an Si (110) substrate which was coated with SiO$_2$ was investigated. Furthermore, we try to understand the role of Si orientation on the alignment of Si$_3$N$_4$. The results showed that crystalline α-Si$_3$N$_4$ microfibers in aligned arrays with a length more than 2 mm are mainly formed along a unique direction of Si <110> on Si (110).

2. Materials and Methods

In this work, a 50 nm thick SiO$_2$ film grown on a two inch Si (110) wafer was used as substrate. Growth of the SiO$_2$ film was performed at 300 °C by plasma-enhanced chemical vapor deposition using a gas mixture of SiH$_4$, N$_2$O, and Ar. After the deposition of SiO$_2$, the substrate was cut to pieces about 1 × 1 cm$^2$. Nitridation of the SiO$_2$/Si (110) substrate with a gas mixture of N$_2$ and H$_2$ was performed in a microwave (2.45 GHz) plasma system, which was commonly employed for chemical vapor deposition of diamond [20,21]. The flow rate of N$_2$ and H$_2$ was 285 and 15 sccm, respectively. The microwave power was set at 700 W and a pressure of 5.3 × 10$^3$ Pa. The nitridation was carried out for 10 and 20 min. The substrate temperature during plasma nitriding was estimated to be in the range of 800–1000 °C as measured by optical pyrometer (wavelength of 0.96 µm).

Raman spectroscopy was carried out in a Horiba Jobin Yvon LabRAM HR 800 spectrometer with 50 mW Ar laser (λ = 533 nm). Scanning electron microscopy (SEM, JEOL JSM-6500F, Tokyo, Japan) was performed to examine surface morphologies of the SiO$_2$/Si (110) substrates. Cross-sectional scanning transmission electron microscopy (ARM200F, JEOL, Tokyo, Japan) with high-resolution transmission electron microscopy (HRTEM) was performed for crystallographic evaluation. Cross-sectional STEM specimen preparation was performed in a dual-beam focused ion beam (FIB, TESCAN LYRA3) system. Before FIB cutting, a 50 nm thin layer of amorphous carbon (a-C) and a 240 nm layer of platinum (Pt) were deposited on the nitride sample surface with an electron beam, followed by deposition of a 250 nm layer of a-C and a 300 nm layer of Pt with ion beam as protective coating.

3. Results

Figure 1a shows a typical SEM micrograph of the nitrided SiO$_2$/Si (110) substrate after 10 min nitriding. The surface morphology shows that Si$_3$N$_4$ crystallites exhibit a fiber-like characteristic with an average diameter of about 1–2 µm and a length of >0.1 mm. Those Si$_3$N$_4$ microfibers are predominately aligned in parallel with each other and approximately along the specific direction of Si [110]. For 20 min nitridation, the length of the microfibers can be as long as 2 mm and the diameter can increase to 5–10 µm, as shown in Figure 1b,c. A few areas on the nitrided substrate are covered with highly dense microfibers. The microfibers shown in Figure 1c exhibit a prism-like morphology, and most of the microfibers are aligned nearly with their longitudinal directions Si [110] in addition to a few deviated ones. The faceted morphology suggests that the microfibers are of the crystalline phase. Furthermore, X-ray energy dispersive spectroscopy shows that those microfibers consist of Si and N, as shown in Figure 1d, with the absence of O, implying that SiO$_2$ may not exist anymore after nitriding.

Raman spectra from different areas on the SEM images shown in Figure 1 were acquired in micromode. A typical Raman spectrum acquired from the microfibers is shown in Figure 2 from 150 to 450 cm$^{-1}$. The Raman peaks observed at 259 and 363 cm$^{-1}$ are identified to belong to α-Si$_3$N$_4$ [22]. The Raman peak at 300 cm$^{-1}$ is the characteristic signal of Si in second order [23,24]. As no β-Si$_3$N$_4$ characteristic peaks are observed, it is evident that all the microfibers are of the α-Si$_3$N$_4$ phase. On the bare area without coverage of the Si$_3$N$_4$ crystallites as shown in Figure 1b, neither Si$_3$N$_4$ nor SiO$_2$ Raman signals can be observed, implying that SiO$_2$ after nitridation might transform to Si$_3$N$_4$, or be etched away by the plasma containing hydrogen. Many of the glass vibrations are
known to occur between 400–700 cm\(^{-1}\) (bridging Si-O-Si vibrations) which are not seen in the spectrum [24].

**Figure 1.** SEM surface morphology after nitriding for (a) 10 min and (b) 20 min. (c) Enlarged view of a dense region. (d) EDS spectrum of microfibers.
Figure 1. SEM surface morphology after nitriding for (a) 10 min and (b) 20 min. 

Figure 3 shows typical cross-sectional TEM/STEM images from the nitried sample for 20 min nitridation after tilting about 7° away from the Si [110] zone axis with the edge-on orientation for the Si$_3$N$_4$/Si interface. Figure 3a,b show low-magnification annular bright field (ABF) and annular dark field (ADF) images in diffraction and atomic number contrast, respectively. As can be seen, the Si$_3$N$_4$ thickness is varied from 70 to 270 nm, and no interlayers exist between Si$_3$N$_4$ and Si. Figure 3c shows a typical high-resolution TEM (HRTEM) image taken from the central region in Figure 3a where the thickness is about 270 nm after tilting about 2° away from the Si [110] zone axis to align Si$_3$N$_4$ in [210] the zone axis. The HRTEM image shows that Si$_3$N$_4$ is in direct contact with Si though the interface between them is not flat. The corresponding fast Fourier transform (FFT) pattern from Si$_3$N$_4$ shown in the upper inset demonstrates that Si$_3$N$_4$ is an α-phase in [210] the zone axis, whereas the Si FFT pattern shown in the lower inset is deviated from the [110] zone axis. Nevertheless, it can still recognize the pattern characteristics of Si with those reflections to understand the essential orientations with respect to Si$_3$N$_4$ ones. Furthermore, an atomic resolution ADF STEM image, as shown in Figure 3d, with the corresponding FFT pattern of Si$_3$N$_4$ in [210] zone axis reveals detailed information at the interface where the Si$_3$N$_4$ lattice can have a reasonably good match with the Si one, i.e., [100] interplanar spacing of 0.672 nm is correspondingly matched with two Si [111] ones of 0.628 nm, implying that there may exist a specific orientation relationship between Si$_3$N$_4$ with Si. In addition, it is seen that the zone axis of α-Si$_3$N$_4$ [210] is approximately parallel to Si [110] with about 2° deviation, suggesting that the lattice mismatch along such a direction is small. The small lattice mismatch can be understood as α-Si$_3$N$_4$, has lattice parameter $a = 7.765$ Å in [210], and the magnitude of the Si [110] direction is 7.681 Å. Linear fits yield the Young’s modulus, $E = 339$ GPa, and the Poisson’s ratio, $\nu = 0.32$ [25].
4. Discussion

From the above results, a number of issues on Si$_3$N$_4$ formation will be discussed, including orientation and phase on Si substrate (110) versus (111) the role of SiO$_2$, plasma condition for nitridation, and fiber morphology.

Though Raman spectra and TEM examinations clearly show the formation of crystalline α-Si$_3$N$_4$, no Si$_3$N$_4$ diffraction peaks from the samples can be observed in acquired θ-2θ X-ray diffraction (XRD) patterns in the range of 10–90°, implying that those microfibers are in a large inclined angle away from those diffraction reflections of low indices, such as 10$ar{1}$0, 10$ar{1}$1, 11$ar{2}$0, 20$ar{2}$1, and 0002. From the FFT patterns of α-Si$_3$N$_4$ in Figure 3, 10$ar{1}$1 reflection is deviated about 7° from the Si surface normal, such that its diffraction signal could not be detected in general θ-2θ XRD scan.

Figure 3. (a,b) Low magnification cross-sectional STEM–ABF and ADF images of α-Si$_3$N$_4$ on Si, respectively; (c) HRTEM image of the Si$_3$N$_4$/Si interface from the central region in (a) with the corresponding FFT patterns of α-Si$_3$N$_4$ and Si; (d) Atomic resolution STEM-ADF image of the α-Si$_3$N$_4$/Si interface with the corresponding FFT pattern of α-Si$_3$N$_4$ in zone axis [1120].
It is known that α-to-β transformation takes place at high temperatures (~1900 °C) and the process is irreversible. It has been shown that β-Si₃N₄ is thermodynamically more stable than α-Si₃N₄ up to 2000 K [26], and α-Si₃N₄ is a metastable phase under ordinary pressure. However, plasma nitridation can be considered as a nonequilibrium condition to form α-Si₃N₄. Therefore, it might be the dominant phase for the short time of nitridation. Currently, it is not known why the formation of only α-Si₃N₄ occurs on Si (110), while both α- and β phases are formed on Si (111), even if the surface energy of Si (110) is higher than Si (111), which might lead to a lower energy barrier for α-Si₃N₄ nucleation [27]. However, it is worth pointing out that most of previous studies on nitridation for formation of Si₃N₄ nanowires and fibers show only an α-phase formed [15,28].

Direct nitridation of bare Si substrate without SiO₂ under the same plasma condition for 20 min shows no nitride formation, as no Raman signals can be observed and SEM observations show that the surface of the Si substrate remains to be as smooth as that before nitridation. Si₃N₄ formation is slow for nitridation of Si and the thickness formed is only a few nanometers after long-time nitriding, while the nitridation rate is faster with SiO₂ to form a thicker nitride film [29]. Thus, it is likely that the reaction of Si with N from the plasma will be retarded with the presence of H in plasma, and it might require an extended period of plasma nitridation to obtain Si₃N₄.

For thermal nitridation, Si and SiO₂ can react to form SiO gas species which then react with nitrogen for nitride formation as the following reactions of (1) and (2) [30].

\[
\text{Si}_3(s) + \text{SiO}_2(s) \rightarrow 2\text{SiO}_2(g) \\
6\text{SiO}_2(g) + 8\text{N}_2(g) \rightarrow 2\text{Si}_3\text{N}_4(s) + 3\text{O}_2(g)
\]

It has been reported that silicon oxide can be nitrided easily below 700 °C using nitrogen plasma generated by electron impact and a large amount of nitrogen can be incorporated in the oxide [5,31]. As most of the gas phases for nitridation can be effectively decomposed in the microwave plasma, there may be plenty of atoms, radicals, and ions as reactive species which can be available for the reactions on the substrate surface. The chemical reactions might occur with a faster rate under the microwave plasma condition. In addition, microwave plasma with H can effectively reduce SiO₂ to Si which then reacts with N. In particular, atomic hydrogen may play a critical role on nitridation. The diffusion rate of atomic hydrogen from the plasma might be faster than that of nitrogen toward the SiO₂/Si interface to delaminate the oxide layer, whereas hydrogen can reduce the oxide surface to expose the bare Si surface which may have a slow reaction with N in comparison with the SiO reaction with N to form Si₃N₄ [32,33]. The accelerated nitriding rates due to the interaction of hydrogen with native oxide on the surface of the Si particles were observed in previous studies [34,35]. Similarly, SiO₂ can be transformed to Si₃N₄ by N₂/H₂ microwave plasma in the present case. In addition, it can be seen that pure N₂ plasma nitridation of SiO₂ may result in the formation of SiON instead of Si₃N₄.

Nitridation of Si (110) has been previously investigated. Saranin et al. reported that the Si(110) surface after thermal nitridation by NH₃ gas in the temperature range of 560–1050 °C is covered with epitaxial islands of Si-nitride in a thickness less than 1 nm, followed by layer-by-layer growth [36]. Higuchi et al. also reported that high-quality Si₃N₄ film in a thickness < 5 nm was formed by nitridation of the Si(110) surface at 600 °C using radical NH [5]. Also, nitridation of Si(110) under RF plasma and the thermal process forms a very thin (10T1) α-Si₃N₄ epitaxial layer [37]. In contrast, the present work shows that on Si (110), the α-Si₃N₄ microfibers only align along with the single direction of Si [1\overline{1}0] after nitridation by microwave plasma. Though the exact mechanism for α-Si₃N₄ formation is not currently known, it may be of interest to understand the relationship from the crystallography point of view. While SiO₂ can be decomposed by N₂/H₂ plasma, the nucleation and growth of Si₃N₄ could be fast along Si <110> due to low strain energy from the small lattice mismatch between them along Si <110> and Si₃N₄ <1\overline{1}20>.

\[
\text{Si}(s) + \text{SiO}_2(s) \rightarrow 2\text{SiO}_2(g) \\
6\text{SiO}_2(g) + 8\text{N}_2(g) \rightarrow 2\text{Si}_3\text{N}_4(s) + 3\text{O}_2(g)
\]
Nitridation of Si and SiO\textsubscript{2} to form nanowires and nanofibers were previously reported. Ramesh and Rao reported formation of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} fibers by carbothermal reduction and nitridation reaction of SiO\textsubscript{2} with N\textsubscript{2} gas at 1623K [38]. Also, a few reports have shown synthesis of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nanowires by nitriding nanocrystalline Si powder at 1623K [38]. Also, a few reports have shown synthesis of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nanowires by nitriding nanocrystalline Si powder at 1623K [38]. Kim et al. demonstrated synthesis of silicon nitride nanowires directly from the silicon substrates via a catalytic reaction under ammonia or hydrogen flow at 1200 °C, using Ga, GaN, and Fe nanoparticles as catalysts [29]. However, those nanowires are randomly distributed. Formation of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} whiskers by nitridation have been also reported by previous studies [35,40,41]. The synthesis of Si\textsubscript{3}N\textsubscript{4} nanowires from the reaction of Si nanoparticles with N\textsubscript{2} in the temperature range of 1200–1440 °C is also reported [42–44]. Ordered arrays of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nanowires have been also synthesized at 1150 °C with NH\textsubscript{3} [45,46]. Direct synthesis of \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nanowires from silicon monoxide on alumina with N\textsubscript{2}/H\textsubscript{2} was also reported [47]. Similarly, it has been demonstrated that single-crystalline \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nanowires can grow in a direction perpendicular to the wet-etched trenches in the SiO film on the plane of the Si substrate without metal catalysis [33].

5. Conclusions

Microwave plasma nitriding of 50 nm SiO\textsubscript{2} on Si(110) substrate using a gas mixture of H\textsubscript{2} and N\textsubscript{2} can form aligned microfibers of crystalline \(\alpha\)-Si\textsubscript{3}N\textsubscript{4} nearly along with Si [110]. The formed Si\textsubscript{3}N\textsubscript{4} microfibers can have a length as long as 2 mm with a diameter of 5–10 \(\mu\)m. Cross-sectional STEM examinations reveal that Si\textsubscript{3}N\textsubscript{4} directly forms on Si without any residual SiO\textsubscript{2} after nitriding. Furthermore, it is shown that most of the microfibers have their longitudinal direction along Si\textsubscript{3}N\textsubscript{4} <11\overline{2}0>, which is approximately parallel to Si [110].

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References

1. Unal, O.; Petrovic, J.; Mitchell, T. CVD Si\textsubscript{3}N\textsubscript{4} on single crystal SiC: Part I. Characterization and orientation relationship at the interface. J. Mater. Res. 1992, 7, 136–147. [CrossRef]

2. Kim, J.W.; Yeom, H.W. Surface and interface structures of epitaxial silicon nitride on Si(111). Phys. Rev. B 2003, 67, 035304. [CrossRef]

3. Riley, F.L. Silicon Nitride and Related Materials. J. Am. Ceram. Soc. 2004, 83, 245–265. [CrossRef]

4. Murakawa, S.; Ishizuka, S.-I.; Nakanishi, T.; Suwa, T.; Teramoto, A.; Sugawa, S.; Hattori, T.; Ohmi, T. Depth Profile of Nitrogen Atoms in Silicon Oxynitride Films Formed by Low-Electron-Temperature Microwave Plasma Nitridation. Jpn. J. Appl. Phys. 2010, 49, 091301. [CrossRef]

5. Higuchi, M.; Aratani, T.; Hamada, T.; Shinagawa, S.; Nohira, H.; Ikenaga, E.; Teramoto, A.; Hattori, T.; Sugawa, S.; Ohmi, T. Electric Characteristics of Si3N4Films Formed by Directly Radical Nitridation on Si(110) and Si(100) Surfaces. Jpn. J. Appl. Phys. 2007, 46, 1895–1898. [CrossRef]

6. Seino, T.; Matsuura, T.; Murota, J. Atomic-order nitridation of SiO2 by nitrogen plasma. Surf. Interface Anal. 2002, 34, 451–455. [CrossRef]

7. Sahu, B.B.; Yin, Y.; Han, J.G. Effect of plasma parameters on characteristics of silicon nitride film deposited by single and dual frequency plasma enhanced chemical vapor deposition. Phys. Plasmas 2016, 23, 033512. [CrossRef]
39. Wang, Q.; Cong, R.; Li, M.; Zhang, J.; Cui, Q. A simple method to synthesize α-Si3N4, β-SiC and SiO2 nanowires by carbothermal route. *J. Cryst. Growth* **2010**, *312*, 2133–2136. [CrossRef]

40. Gedevanishvili, S.; Cherian, K.; Agrawal, D.; Roy, R. Synthesis of Silicon Nitride Whiskers by Microwave Heating. *MRS Proc.* **1998**, *547*, 13. [CrossRef]

41. Chen, F.; Li, Y.; Liu, W.; Shen, Q.; Zhang, L.; Jiang, Q.; Lavernia, E.J.; Schoenung, J.M. Synthesis of α silicon nitride single-crystalline nanowires by nitriding cryomilled nanocrystalline silicon powder. *Scr. Mater.* **2009**, *60*, 737–740. [CrossRef]

42. Farjas, J.; Pinyol, A.; Rath, C.; Roura, P.; Bertran, E. Kinetic study of the oxide-assisted catalyst-free synthesis of silicon nitride nanowires. *Phys. Status Solidi* **2006**, *203*, 1307–1312. [CrossRef]

43. Wang, F.; Qin, X.; Yang, L.; Meng, Y.; Sun, L. Synthesis and photoluminescence of Si3N4 nanowires from La/SiO2 composites and Si powders. *Scr. Mater.* **2009**, *60*, 737–740. [CrossRef]

44. Tian, Z.; Chen, K.; Sun, S.; Zhang, J.; Cui, W.; Xie, Z.; Liu, G. Synthesis of Si3N4 nanowires by catalyst-free nitridation of (Si + SiO2) mixture. *Micro Nano Lett.* **2019**, *14*, 919–921. [CrossRef]

45. Ahmad, M.; Zhao, J.; Zhang, F.; Pan, C.; Zhu, J. One-step synthesis route of the aligned and non-aligned single crystalline α-Si3N4 nanowires. *Sci. China Ser. E Technol. Sci.* **2009**, *52*, 1–5. [CrossRef]

46. Ahmad, M.; Zhao, J.; Pan, C.; Zhu, J. Ordered arrays of high-quality single-crystalline α-Si3N4 nanowires: Synthesis, properties and applications. *J. Cryst. Growth* **2009**, *311*, 4486–4490. [CrossRef]

47. Cui, J.; Li, B.; Zou, C.; Zhang, C.; Wang, S. Direct Synthesis of α-Silicon Nitride Nanowires from Silicon Monoxide on Alumina. *Nanomater. Nanotechnol.* **2015**, *5*, 32. [CrossRef]