Catalytic Effects of Cr on Nitridation of Silicon and Formation of One-dimensional Silicon Nitride Nanostructure

Feng Liang1, Lilin Lu1, Liang Tian1, Faliang Li1, Haijun Zhang1 & Shaowei Zhang1,2

The catalytic effects of chromium (Cr) on the direct nitridation of silicon (Si) and morphology of nitridation product were investigated. Cr dramatically improved the conversion of Si to silicon nitride (Si3N4). The complete conversion was achieved at 1350 °C upon addition of 1.25 wt% Cr. This temperature was much lower than that required in the case without using a catalyst. Meanwhile, Cr played an important role in the in-situ growth of one-dimensional (1-D) α-Si3N4 nanostructures. α-Si3N4 nanowires and nanobelts became the primary product phases when 5 wt% Cr was used as the catalyst. The growth processes of the 1-D α-Si3N4 nanostructures were governed by the vapor-solid mechanism. First-principle calculations suggest that electrons can be transferred from Cr atoms to N atoms, facilitating the Si nitridation.

Silicon nitride (Si3N4) possesses many superior properties, in particular, excellent thermal shock resistance, mechanical properties and chemical stability at both room and high temperatures1,2. Therefore, Si3N4 based materials are extensively used in a variety of areas such as in chemical reaction vessels, heat exchanger bearings, engine and gas turbines, high-temperature components, automotive parts, and aerospace vehicles3,4.

Several methodologies and techniques have been developed to produce Si3N4 powders from siliceous raw materials, including carbothermal reduction nitridation of silica5,6, chemical vapor deposition7–9, direct nitridation of silicon (Si)10, sol-gel processing11,12, and combustion synthesis13,14. Among these, the direct nitridation of Si powder is regarded as a low-cost and straightforward route for the large scale production of Si3N4 powder and bulk Si3N4 based materials. Unfortunately, with this technique, much unreacted Si often remains in the final products, due to partial Si melting caused by the high nitridation temperature used and additional heat released from the strong exothermic reaction between Si and nitrogen.

One of the strategies considered previously to address this issue was use of a suitable catalyst for the Si nitridation process. So far, catalytic effects of several metals on the kinetics of Si nitridation, α-β-phase ratio and product morphology have been investigated15–20. Among the non-transition metals tested, only calcium (Ca) showed some accelerating effect on the conversion from Si to Si3N4 and the formation of α-Si3N4. On the other hand, among the transition metals, cobalt (Co) was found to show significant accelerating effects on the Si nitridation and in-situ growth of α-Si3N4 nanorods or nanowires21. Nevertheless, when it is used as a catalyst, low melting Co and/or Co-Si alloy phases will remain after the nitridation, which could potentially deteriorate high-temperature properties of the final product materials22,23. Therefore, it is necessary to use other alternative metal catalysts to overcome this problem.

One of the candidate metal catalysts for this could be chromium (Cr). Cr, chromium nitride and CrxSiy phases all have high melting points and good high temperature properties24–26. Therefore, their remaining after the nitridation would not have much negative effects on high temperature properties of the final product materials. However, whether Cr is catalytically active in the Si nitridation is still in controversy. Cofer and Lewis27 claimed that Cr could accelerate the Si nitridation via promoting the dissociative chemisorption of nitrogen. On the other hand, according to Pavarjarn et al.15, Cr actually had no obvious effect on the Si nitridation even at 1300 °C.

1 The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China. 2 College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, U.K. Correspondence and requests for materials should be addressed to H.Z. (email: zhanghaijun@wust.edu.cn) or S.Z. (email: s.zhang@exeter.ac.uk)
In the present work, the effects of Cr with various addition levels (up to 10%) on the direct nitridation of Si were investigated, and morphologies of Si$_3$N$_4$ products examined in detail. To assist understanding the role played by Cr in the nitridation process, first-principle calculations were also carried out. The experimental and calculated results were discussed, based on which, the relevant catalytic reaction mechanisms proposed.

**Results**

**Effects of Cr additions on Si nitridation.** Figure 1 illustrates the effects of Cr content on the overall conversion (OC) of Si and α-phase contents in samples resultant from 3 h nitridation at different temperatures. At 1200 °C and 1250 °C, the OC of Si to Si$_3$N$_4$ in the reference samples without Cr was low (Fig. 1a). However, it increased evidently with increasing the Cr content. For example, at 1250 °C, the OC was only ~21% in the case of no Cr addition, but increased significantly to ~66% in the sample containing 10 wt% Cr. Upon further increasing the temperature to 1350 °C, the OC in the reference sample increased to 91% whereas nearly all of the Si had been nitrided in the sample containing 1.25 wt% Cr. Figure 2 shows XRD patterns of samples containing 0–10% Cr after 3 h nitridation at 1250 °C and 1350 °C, respectively.

Figure 1. Effects of Cr content on (a) the overall conversion of silicon and (b) the formation of α-phase in samples resultant from 3 h nitridation at different temperatures.

Figure 2. XRD patterns of samples containing various amounts of Cr: (a) 0, (b) 1.25, (c) 2.5, (d) 5, (e) 7.5, and (f) 10 wt%, after 3 h nitridation at 1250 °C and 1350 °C, respectively.

In the present work, the effects of Cr with various addition levels (up to 10%) on the direct nitridation of Si were investigated, and morphologies of Si$_3$N$_4$ products examined in detail. To assist understanding the role played by Cr in the nitridation process, first-principle calculations were also carried out. The experimental and calculated results were discussed, based on which, the relevant catalytic reaction mechanisms proposed.
α- and β-Si₃N₄ were identified in the reference sample, along with some unreacted Si. On the other hand, in the sample containing 1.25 wt% Cr, Si disappeared and only α- and β-Si₃N₄ phases were present, indicating the complete conversion from Si to Si₃N₄. On increasing Cr to ≥5 wt%, α- and β-Si₃N₄ remained as the primary phases, however, minor Cr₃N and two other impurity phases (appeared to be Cr₃Si and Cr₅Si₃) were detected.

Shown in Fig. 3 are SEM images of samples after 3 h nitridation at 1350 °C. Some unreacted Si was identified in the reference sample without Cr by EDS (the inset 1 in Fig. 3a), which was consistent with the XRD results shown in Fig. 2b, and a few one-dimensional (1-D) nanostructural phases were occasionally seen in the sample. EDS (the inset 2 in Fig. 3a), along with the XRD results (Fig. 2b), confirmed that the crystalline phases surrounding the unreacted Si were Si₃N₄, suggesting that the nitridation of Si particles proceeded from the surface towards the center. Compared to the reference sample, much less unreacted Si phases but much more Si₃N₄ phases were identified by EDS (the insets in Fig. 3b–d) in the samples containing Cr. Furthermore, with increasing the Cr content from 1.25 to 5 wt%, the quantity of 1-D nanophases also increased evidently.

High-magnification SEM images (Fig. 4) further reveal that most of the 1-D nanophases actually possessed wire-, belt- and branched belt-like morphologies. The nanowires were 50–200 nm in diameter and about 50 μm in length, and the nanobelts were 300–1000 nm in width and about 10 μm in length. However, upon addition of >5% Cr, the quantity of 1-D nanowires/nanobelts appeared to be decreased and more Si₃N₄ particles coexisted with them.

Figure 5 further presents TEM, HRTEM, EDS and SAED of a representative nanowire formed in the sample containing 5 wt% Cr, after 3 h nitridation at 1350 °C, showing smooth surface and uniform diameter of the nanowire (Fig. 5a). EDS (Fig. 5b) further revealed that the nanowire contained Si and N in the atomic ratio of 0.751, almost the same as the stoichiometric ratio (0.750) of Si₃N₄ (Cu peaks were from the copper grid sample holder), verifying that it was Si₃N₄. Also SAED (Fig. 5c) confirmed that it was single-crystal α-Si₃N₄. In addition, two-dimensional lattice fringes with d-spacing values of 0.56 nm and 0.67 (Fig. 5d) matched with the (001) and (100) planes, respectively, suggesting that the α-Si₃N₄ nanowire grew along the [001] direction.

Apart from Si₃N₄ nanowires, as mentioned above, many nanobelts were also formed in the Cr added samples. As revealed by TEM (Fig. 6a), they had different widths but their widths were uniform along the entire length. EDS (Fig. 6b), SAED (Fig. 6c) and HRTEM (Fig. 6d) identified that they were also single crystal α-Si₃N₄ but were grown along the [101] direction. It should be pointed out that no particles were observed and no Cr was detected by EDS at tips of the 1-D Si₃N₄ nanowires and nanobelts (Figs 5b and 6b), suggesting that their growth processes.
should not have been dominated by the well-established vapor-liquid-solid (VLS) tip-growth mechanism. The detailed growth mechanism regarding this will be discussed in more detail in Section 3.3 below.

In order to illustrate the role of Cr in the formation of these nanostructure materials, TEM images of the fired sample containing 10 wt% Cr were also taken. As shown in Fig. 7a, two types of α-Si₃N₄ nanostructures, i.e. nanowire with 100 nm in diameter and nanobelt with 400 nm in width, simultaneously grew from a particle. EDS analysis (insets in Fig. 7b,c) confirmed that the main parts and tips of the 1-D nanostructures contained only Si and N.

Figure 4. High-magnification SEM of the 1-D nanostructures formed in the sample containing 5 wt% Cr: (a) nanowires and (b) nanobelts, after 3 h nitridation at 1350 °C.

Figure 5. TEM images of the 1-D α-Si₃N₄ nanostructures in the sample containing 5 wt% Cr after 3 h nitridation at 1350 °C: (a) a typical low-magnification TEM image of a representative the α-Si₃N₄ nanowires, (b) corresponding EDS spectrum and (c) SAED pattern of the nanowire, and (d) an HRTEM image of the α-Si₃N₄ nanowire (the area A in Fig. 5a).
N, but no Cr. Interestingly, Cr element was only detected at the root of the 1-D nanostructures (by EDS, Fig. 7d), which is believed to have acted as a “catalyst center” for the nucleation of the 1-D α-Si$_3$N$_4$ nanostructures.

Mechanism of Cr catalyzed nitridation. The results presented and discussed above (Figs 1~7) suggested that Cr had played significant roles in accelerating the Si nitridation. To assist clarifying these roles, DFT calculations at the GGA-PBE/USP level of theory were carried out to simulate the adsorption behavior of a N$_2$ molecule onto the Cr (001) surface and study the catalytic mechanism of Cr catalyst for nitridation reaction. The adsorption energy (E$_{ad}$) of N$_2$ on the para-position (90.24 kJ/mol) of the Cr (001) surface is higher than that on the ortho-position (66.24 kJ/mol) (Table 1), suggesting that adsorption of N$_2$ onto the former is more favorable than the latter. Moreover, the bond lengths in a N$_2$ molecule adsorbed on the para- and ortho-positions of Cr (001) surface are respectively 1.176 and 1.195 Å, which are longer than the original bond length (1.158 Å) in a free-standing N$_2$ molecule (Table 1). Such increase in the bond length of N$_2$, is believed to have assisted the dissociation of N$_2$, as discussed previously.

The Mulliken atomic charge distributions of N and Cr atoms (Fig. 8 and Table 1) reveal that the N atoms are indeed negatively charged, whereas the Cr atoms are positively charged, providing further evidences on the electronic charge transfer from the latter to the former. In the case of para-position absorption, the two N atoms in a N$_2$ molecule possess identical electronic charge. Moreover, the two N atoms absorbed on the ortho-position of Cr (001) surface have negligibly different negative-charges, due to the asymmetrical surrounding of the two N atoms, as also reported in our previous paper. Since the Π$_{2p}$ molecular orbital is an anti-bonding level, the bonding strength in a N$_2$ molecule will be weaken if the adsorbed N$_2$ molecule receives an electron from a Cr atom in the p-state. Changes in both bond length and Mulliken charge suggest that the N≡N bond can be weakened and the relatively stable N$_2$ molecule activated when it is absorbed onto the surface of Cr.

Discussion
As well documented in the literature, the catalytic growth of 1-D nanostructure is generally controlled by the well-established VLS mechanism. The presence of a catalyst particle at the tip of a nanowire/nanorod/nanotube is often regarded as one of the main supportive evidences for this mechanism. In the present work, Cr was found at the roots of the 1-D α-Si$_3$N$_4$ nanostructures, suggesting that Cr had played dominant roles in the nucleation of α-Si$_3$N$_4$ and the subsequent growth of the 1-D nanowires and nanobelts (Fig. 4). The detailed mechanisms can be
schematically illustrated in Fig. 9. For the case of 1-D $\alpha$-Si$_3$N$_4$ nanostructures, in the initial stage, N$_2$ molecules diffused onto the surfaces of Cr particles (Fig. 9a). As predicted by the first-principle calculations (Section 3.2), the bond length in the N$_2$ molecules would be increased and the bond strength decreased after their adsorption onto the Cr particles (see Fig. 8), resulting in activated N$_2$ molecules. Subsequently, such N$_2$ molecules would react with Si vapor generated from Reaction (1) (Fig. 9b-1), forming Si$_3$N$_4$ which would nucleate forming “crystal seeds” (Reaction (2)) on the surface of Cr (Fig. 9c-1). Owing to the hexagonal structure of Si$_3$N$_4$ (i.e., cell parameters $a = b \neq c$), its different planes exhibit different surface energy values (J/m$^{-2}$), for example, $E(110)$: 1.95; $E(010)$: 2.57; $E(001)$: 2.74; and $E(101)$: 2.77. In this case, crystal surfaces with lower energies tend to serve as the enclosure surfaces, so the incoming Si and N preferred to diffuse to and deposit on the high energy surfaces (001) and (101) in the length directions [001] and [101], respectively, resulting in simultaneous formation of nanowires and nanobelts (Fig. 9d-1,e-1, Figs 5 and 6). Considering that the residual Cr catalyst was only detected in the roots of the nanostructures (Fig. 7) rather than at their tips, the VS mechanism should have dominated the growth process of the 1-D nanostructures.

Nevertheless, upon addition of $>5\%$ Cr, lots of Si$_3$N$_4$ particles rather than Si$_3$N$_4$ nanowires/nanobelts were formed in the samples (Figs 2 and 3), which can be explained by the following two reasons: 1) the formation of lots of Cr$_x$Si$_y$ alloy in the sample (Fig. 2) delayed the growth of 1-D $\alpha$-Si$_3$N$_4$ (Fig. 3d) as a result of the low activation energy of nitrogen diffusion through the alloy$^{31}$, and 2) when the N$_2$ molecules diffused onto the Cr-Si interface (Fig. 9b-2), they would be activated by Cr forming active nitrogen species, thus accelerating the nitridation process.

**Figure 7.** TEM images of the sample containing 10 wt\% Cr: (a) A low-magnification TEM image of 1-D $\alpha$-Si$_3$N$_4$ nanostructures which had just started to grow, (b,c) HRTEM images and corresponding EDS spectra (inset) of the 1-D $\alpha$-Si$_3$N$_4$ nanostructures, detected from the areas A and B respectively in Fig. 7a, and (d) EDS of the root of 1-D $\alpha$-Si$_3$N$_4$ nanostructures (highlighted by the dotted ring in the Fig. 7a).

**Table 1.** Electronic charge on N atoms, N-N bond length, and adsorption energy of N$_2$ molecule on Cr (001) surface based on the first-principle calculations.

|                | Electronic charge | Bond length (Å) | $E_{ad}$ (kJ/mol) |
|----------------|-------------------|-----------------|-------------------|
| Free-standing N$_2$ molecule | 0.00, 0.00         | 1.158           | —                 |
| N$_2$ adsorbed on para-position Cr atoms | $-0.04, -0.04$         | 1.176           | 90.24             |
| N$_2$ adsorbed on ortho-position Cr atoms | $-0.07, -0.01$         | 1.195           | 66.24             |
rate of Si. With increasing the Cr addition, more activated N₂ molecules would be generated at the interface (Fig. 9c-2). Consequently, the nitridation of Si would be promoted via a gas-solid reaction process (Reaction (3)), and more Si₃N₄ particles generated via isotropic formation from Si surface to the center (Fig. 9d-2).

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

In summary, Cr exhibited a strong accelerating effect on the conversation of Si to Si₃N₄. At 1350 °C, the complete conversion of Si to Si₃N₄ was achieved in the samples containing 1.25 wt% Cr. When the Cr addition was 5 wt%, the catalyst efficiently promoted the formation of 1-D α-Si₃N₄ nanostructures. Si₃N₄ nanowires about 50 μm long and 50–200 nm in diameter, and nanobelts about 10 μm long and 300–1000 nm in width, were simultaneously obtained. The 1-D α-Si₃N₄ nanostructures grew from their Cr-containing roots via a VS mechanism. The accelerating effect of Cr on the nitridation of Si powder can be ascribed to the electron transfer from Cr to N, increasing the bond length and weakening bond strength in N₂ molecules, as predicted by the first-principle calculations.

Methods

Raw materials and sample preparation. Si (99.9% pure, ≤44 μm, Naiou Nano Technology Co., Ltd., Shanghai, China) and Cr powders (≤6 μm, 99.9% pure, Naiou Nano Technology Co., Ltd., Shanghai, China) were used as the main starting materials, and high purity N₂ (purity >99.999%) was used as the nitrogen source. Si powders were mixed with various amounts of Cr (0–10 wt%) for 30 min in a ball mill at 300 rpm. The mixed batch was pressed under 30 MPa forming cylindrical samples with 20 mm in height and 20 mm in diameter. The samples were placed in an alumina-tube furnace and fired at 1200–1350 °C for 3 h in flowing N₂. As the nitridation reaction of Si is strongly exothermic, to avoid overheating induced Si melting and its negative effect in nitridation, the furnace was initially heated to 1150 °C and then 1280 °C and held at each of these temperatures for 1 h, before being further heated to the final target nitridation temperature.

Sample characterization. Phase compositions in reacted samples were determined by X-ray diffraction (XRD, X’Pert Pro, Philips, Netherland). Spectra were recorded at 40 kV and 40 mA using Cu-Kα radiation, with
a scanning rate of 2° (2θ)/min and a step size of 0.02° (2θ). ICDD cards used to identify Si, α-Si₃N₄ and β-Si₃N₄ are No. 01-089-5012, 01-073-1210 and 01-082-0697, respectively. The Rietveld refinement method was used to calculate crystalline phase contents in the fired samples. The overall conversion (OC) from Si to Si₃N₄ was determined using the quantitative analysis values of the Si, α- and β-Si₃N₄, and α-phase contents in final products were calculated based on the quantitative analysis values of the α- and β-Si₃N₄.

Microstructures and morphologies of the final products were observed by using a field emission scanning electron microscope (FESEM, Nova 400 Nano FESEM, FEI Co., USA, 15 kV) and a high-resolution transmission electron microscope (HRTEM, JEM-2000 F, Jeol Ltd., Japan, 200 kV). The samples for SEM were coated with gold, and those for TEM were prepared by ultra-sonic dispersion of the sample powders in EtOH, followed by dropping and drying the suspension onto a copper grid, respectively. Selected area electron diffraction (SAED), along with an energy dispersive X-ray spectroscopy (EDS, Noran 623 M-3SUT, Thermo Electron Corporation, Japan) was used for assisting phase identifications.

First-principle calculation. To assist understanding the catalytic nitridation mechanism in the case of using Cr as a catalyst, first-principle calculations based on the Cr (001) slab model were carried out using the CASTEP program based on the plane-wave pseudopotential (PW-PP) approach32. A vacuum space of 10 Å was introduced to prevent interactions between slabs. The outmost six layers and absorbed N₂ molecules were fully relaxed. The electron-ion interactions were represented by ultrasoft pseudopotentials (USP)33, and the electron-electron interactions were calculated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional34. The equilibrium geometries were obtained by performing geometry optimization using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) minimization method35, the energy cutoff for the plane wave basis set was set at 450 eV, and the Brillouin zone was sampled at 7 × 7 × 1 Monkhorst-Pack k-points. A Fermi smearing of 0.1 eV was utilized to speed up SCF convergence. The applied convergence criteria for geometry optimization were respectively 2.0 × 10⁻⁵ eV/atom, 0.05 eV/Å and 0.002 Å for energy, force and displacement.

References
1. Riley, F. L. Silicon nitride and related materials. J. Am. Ceram. Soc. 83, 245–265 (2000).
2. Klemm, H. Silicon nitride for high-temperature applications. J. Am. Ceram. Soc. 93, 1501–1522 (2010).
3. Mashkoor, A., Jiong, Z., Caofeng, P. & Jing, Z. Ordered arrays of high-quality single-crystalline α-Si₃N₄ nanowires: synthesis, properties and applications. J. Cryst. Growth 311, 4486–4490 (2009).
4. Klemm, H. Silicon nitride for high-temperature applications. J. Am. Ceram. Soc. 93, 1501–1522 (2010).
Catalytic Effects of Cr on Nitridation of Silicon and Formation of One-
Dimensional Silicon Nitride Nanostructure.

Liang, F. et al. Competitive financial interests: The authors declare no competing financial interests.

F. Liang, H.Z. and S.Z. wrote the main manuscript text, L.T., F. Li and L.L. made the DFT calculation and prepared Figures 8. All authors reviewed the manuscript.

Additional Information

How to cite this article: Liang, F. et al. Catalytic Effects of Cr on Nitridation of Silicon and Formation of One-
Dimensional Silicon Nitride Nanostructure. Sci. Rep. 6, 31559; doi: 10.1038/srep31559 (2016).

© The Author(s) 2016