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Microstructure and high temperature oxidation resistance of mixed long Si$_3$N$_4$ nanowires with wide diameter distribution

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Abstract

Herein, the mixed α-Si$_3$N$_4$ nanowires with large diameter differences (35–400 nm) were prepared by repeated re-filling of nitrogen gas during high temperature nitridation, and the length thereof was substantially above 500 μm (the longest length even could reach centimeter level). And there were significant differences in the interplanar spacing and growth direction of α-Si$_3$N$_4$ nanowires with different diameters. Moreover, the high temperature oxidation resistance of nanowires were systematically analyzed and obtained the following results: the oxidation reaction of Si$_3$N$_4$ nanowires became intensified significantly at about 1100 °C, and the diffraction intensity of Si$_3$N$_4$ in XRD patterns decreased with the increase of oxidation temperature until it was substantially oxidized to SiO$_2$ at about 1400 °C; and the changes in the microstructure of Si$_3$N$_4$ nanowires became more intense as the oxidation temperature increased until a significant shrinkage occurred at about 1400 °C, at which point it no longer exhibited a distinct nanowire morphology. The above studies may provide a reference for the further research and application of α-Si$_3$N$_4$ nanowires in the high temperature field.

1. Introduction

The silicon nitride (Si$_3$N$_4$) nanowires are nanomaterials with corrosion resistance, toughness, high tensile strength, wide bandgap (5.3 eV) and photosensitivity, and they can be widely used in the fields of nano-reinforced materials, high-temperature resistant catalyst carriers, nano-lasers, nano-cables, and semiconductor materials [1–7]. In general, the Si$_3$N$_4$ nanowires is carried out by carbothermal reduction method [8], direct nitridation method [9], combustion synthesis method [10] and chemical vapor deposition method [11]. Kim et al [12] and Peng et al [13] synthesized Si$_3$N$_4$ nanowires on silicon wafers by direct nitridation method and pyrolysis precursor method, respectively. Chaudhuri et al [14] prepared Si$_3$N$_4$ nanowires with a diameter of about 500 nm by carbothermal reduction method using silica gel as a raw material, and the length of nanowires could reach 200 μm. In addition, nanomaterials with different structures (i.e., Si$_3$N$_4$ nanobelts [15], Si$_3$N$_4$ nanorods [16] and Si$_3$N$_4$ nanotubes [17, 18]) have also attracted great attention.

It is a hot research topic to combine Si$_3$N$_4$ nanowires with other materials to improve certain properties of materials. Kusunose et al [19] generated β-Si$_3$N$_4$ nanowires in epoxy resin by carbothermal reduction method, and improved the thermal conductivity of the material to 9.2 W·m$^{-1}$·K$^{-1}$ while ensuring the insulation of the material. Fu et al [20] and Ran et al [21] both prepared the nanowire structure with α-Si$_3$N$_4$ nanowire as the inner core and SiO$_2$ as the outer shell, which was an ideal semiconductor-insulator heterostructure and has great potential for application in the field of nano-cables.

Excitingly, Si$_3$N$_4$ nanowires have great potential in high temperature applications, such as aerospace and high temperature catalyst carriers. However, there are few studies on the high temperature oxidation resistance of Si$_3$N$_4$ nanowires. Herein, the well-crystallized Si$_3$N$_4$ nanowires were obtained by a simple and safe high-temperature nitridation method, whose diameters were distributed in a wide range of 35–400 nm, and there were some differences between the crystal structures of Si$_3$N$_4$ nanowires with different diameters. Furthermore, the thermogravimetric analysis of Si$_3$N$_4$ nanowires and their microstructure and composition after high
temperature oxidation were systematically analyzed, which may provide a reference for the study of their application in high temperature fields.

2. Materials and methods

High-purity Si powder (particle size: 3–10 μm, purity >99.9%, China) was used as a raw material. Firstly, The Si powder was placed in crucibles and dried in a vacuum oven at 25 °C for 48 h. Next, the dried Si powder was poured into a graphite box and subjected to incomplete capping treatment (i.e., a part of the void was left in the graphite box to allow N2 to enter). Then the above samples were placed in a high-temperature nitriding furnace, and the furnace was evacuated and then introduced into N2 gas (purity ≥ 99.99%, O2 ≤ 20 ppm) to bring the pressure in the furnace to 0.1 MPa (in order to obtain Si3N4 nanowires, the content of O2 impurities in N2 gas must be kept at a low level). Finally, The samples were nitrided at 1300 °C for 6 h, and the heating rate was set at 2 °C min⁻¹. In the high temperature nitriding process, the nitriding furnace was evacuated every 1 h and refilled with N2 (the purpose was to disturb the gas flow in the nitriding furnace greatly), and the pressure in the furnace was always maintained at ∼0.1 MPa. Moreover, the high-temperature oxidation experiment was performed on the nanowires, i.e., the nanowires were placed in a high-temperature air furnace (∼0.1 MPa) and kept at a certain oxidation temperature (800 °C, 1000 °C, 1200 °C, 1400 °C) for 2 h, and the heating rate was 2 °C min⁻¹.

The thermogravimetric analysis (TG) and differential thermal analysis (DTA) of nanowires were recorded on a simultaneous thermal analyzer (STA2500 Regulus, Germany) with a heating rate of 10 K min⁻¹ (atmospheric conditions: flowing oxygen at a flow rate of 40 ml min⁻¹). The microstructure of nanowires was observed via scanning electron microscopy (SEM, Phenom World Phenom XL, USA) and high resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30, Netherlands). The phase composition of nanowires was measured via x-ray diffractometer (XRD, Bruker D8 advance, Germany) in the range of 10°–45° (the scanning speed was 5 °/min).

3. Results and discussion

3.1. Structural and microstructural

Figures 1(a) and (b) present the white film-like product deposited on the graphite box cover after high temperature nitridation, and the film had a thickness of 0.5–0.9 mm. Figures 2(a)–(d) show SEM micrographs of white film-like products with microstructures of mixed nanowires of different diameters, and the diameter of the nanowires is mainly distributed over a large range of about 35–400 nm.

It can be inferred that the growth of Si3N4 nanowires obtained in this study is consistent with the vapor-solid (VS) growth mechanism [22–24]. During high temperature nitridation, Si reacts with SiO2 attached to its surface and a small amount of O2 in N2 to form gaseous SiO. Then SiO diffuses to the vicinity of the graphite box and is enriched, further reacts with N2 to form Si3N4 and continuously epitaxially grows into nanowires. Moreover, the uneven distribution of the diameter (35–400 nm) of the nanowires can be ascribed to the reaction kinetics. The nanowires are susceptible to external conditions during the growth process, and the perturbation of the N2 gas flow caused by the repeated charging and discharging of N2 gas in the nitriding furnace interferes with the growth process of the nanowires, leading to the formation of Si3N4 nanowires of different diameters. Moreover, the radial growth of nanowires interfered by the nitrogen gas flow is inhibited and tends to grow axially, resulting
in finer nanowires, however, the nanowires with less interference are more stable and eventually grows into thick nanowires.

3.2. Material composition and crystal structure
Figure 3 displays the XRD pattern of the nanowires consists of $\alpha$-$\text{Si}_3\text{N}_4$, and the peak shape of each diffraction peak in the spectrum was quite sharp, implying that the nanowires are well crystallized. Furthermore, the above XRD pattern was calculated and obtained the unit cell parameter where $a$ is 7.7514 and $c$ is 5.6189, which was consistent with the standard map of $\alpha$-$\text{Si}_3\text{N}_4$ numbered JPCDS No. 76–1407.
Figure 4 shows the HRTEM and selected area electron diffraction (SAED) patterns of two typical Si₃N₄ nanowires with different diameters (62 nm and 311 nm). The nanowires having a diameter of 62 nm exhibited lattice fringe spacings (interplanar spacings) of 0.67 nm and 0.43 nm, which corresponded to the (100) and (101) crystal planes of α-Si₃N₄, respectively, and the preferential crystal orientation was [100] (figures 4(a) and (b)). Moreover, the nanowires having a diameter of 311 nm which grew along the growth direction of [110] exhibited the interplanar spacings of 0.34 nm and 0.39 nm (figures 4(c) and (d)). There were significant differences in the interplanar spacing and growth direction of the above two nanowires with different diameters, which may be caused by the different growth processes of nanowires. In addition, the diffraction spots of the SAED patterns of the above nanowires were both lattice-distributed, implying that the nanowires were single crystals with good crystallinity.

3.3. High temperature oxidation of nanowires

Nanowires have some physicochemical properties that are different from bulk structures due to surface effects and size effects. In general, the oxidation resistance of Si₃N₄ materials mainly depends on the oxide layer on the surface, while the Si₃N₄ nanowires make it easier to react with O₂ due to their size effect and higher surface activation energy [25]. Therefore, it is necessary to analyze the high temperature oxidation resistance of Si₃N₄ nanowires.

Figure 5 presents the TG-DTA curves of mixed Si₃N₄ nanowires under flowing oxygen conditions. The DTA curve exhibited a broad endothermic peak at around 400 °C, and the corresponding TG curve basically maintained a horizontal shape, which may be caused by the melting of a small amount of impurities with low melting point on Si₃N₄ nanowires. In the temperature range of 400 °C–1100 °C, the TG curve exhibited a slow upward trend, at which time the Si₃N₄ nanowires underwent a slow oxidation reaction. With the further increasing of temperature, the rising rate of the TG curve was obviously increased, and the corresponding DTA curve exhibited a broad exothermic peak, at which time the oxidation of Si₃N₄ nanowire was intensified.
Furthermore, when the temperature was increased to 1400 °C and 1500 °C, the mass of the nanowires was increased by 20.6% and 27.4%, respectively. Theoretically, if Si₃N₄ is completely oxidized to SiO₂, its weight will increase by 28.6%, which implies that the Si₃N₄ nanowire was substantially completely oxidized to SiO₂ at 1500 °C.

Figure 6 displays the XRD pattern of mixed nanowires with different diameters after high temperature oxidation (800 °C, 1000 °C, 1200 °C, 1400 °C). When the oxidation temperature did not exceed 1200 °C, the composition of the nanowire was always α-Si₃N₄. Moreover, with increasing oxidation temperature, the diffraction peak of α-Si₃N₄ exhibited a significant weakening trend, which can be ascribed to the decrease in the crystallinity of Si₃N₄ nanowires under high temperature oxidation conditions. Furthermore, when the oxidation temperature was increased to 1400 °C, most of the Si₃N₄ nanowires were oxidized to SiO₂, so only the diffraction peak of SiO₂ appeared in the XRD pattern (it verified the results of the TG-DTA analysis of nanowires).

Figure 7 shows the SEM micrograph of nanowires after oxidation at 800 °C, 1000 °C, 1200 °C, 1400 °C, respectively. When the oxidation temperature ranged from 800 °C to 1200 °C, a molten droplet-like structure appeared on the nanowire, and it grew larger with the increase of oxidation temperature (the nanowires still substantially maintained a linear structure). However, when the oxidation temperature was increased to 1400 °C, the nanowires became significant shrinkage and no longer exhibited a distinct linear structure.

4. Conclusion

The mixed α-Si₃N₄ nanowires with large diameter differences were obtained by repeated re-filling of nitrogen gas during high temperature nitridation. The diameter of the nanowires was distributed in a large range of 35–400 nm, and the length of nanowires was basically above 500 μm (the longest was more than 1 mm). And the
results obtained by HRTEM and SAED analysis of typical two Si$_3$N$_4$ nanowires with different diameters implied that there are differences in the interplanar spacing and growth direction of Si$_3$N$_4$ nanowires. In addition, the oxidation reaction of Si$_3$N$_4$ nanowires became intensified significantly at about 1100 °C, and Si$_3$N$_4$ was substantially completely oxidized to SiO$_2$ at about 1500 °C. With increasing oxidation temperature, the diffraction intensity of Si$_3$N$_4$ decreased, and the change in the microstructure of Si$_3$N$_4$ nanowires caused by high temperature oxidation became more intense. When the oxidation temperature was increased to 1400 °C, the Si$_3$N$_4$ nanowires shrunk significantly (no longer had obvious nanowire morphology), which were almost completely oxidized to SiO$_2$. This study found a simple method for the preparation of mixed long α-Si$_3$N$_4$ nanowires with various diameters. And the study of the high temperature oxidation resistance of Si$_3$N$_4$ nanowires after may provide a reference for its application in high temperature field.

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Figure 7. The SEM micrographs of nanowires after oxidation at different high temperatures: (a) 800 °C; (b) 1000 °C; (c) 1200 °C; (d) 1400 °C.
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