

Synthesis of Silicon Nitride Nanowires by Ball Milling and Annealing

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Single-crystal silicon nitride (α -Si₃N₄) nanowires (SiNNWs) have been successfully synthesized in large quantity by ball-milling and annealing method. Pure silicon powder has been ball milled for 150 hours in different atmospheres, and subsequently annealed at 1200 °C for 1 hour. Changing the milling gas from N₂ to NH₃ results in different structures of SiNNWs. The SiNNWs obtained from the N₂-milled Si have a thin amorphous oxide layer, while those produced from NH₃-milled Si have a 'clean' surface with an Fe-rich particle at the nanowire tip. This suggests that these two different kinds of SiNNWs are grown via different mechanisms. The ball milling treatment clearly facilitates growth of crystalline SiNNWs during subsequent annealing. The relationship between milling atmosphere and growth process will be discussed.

1. Introduction

Silicon nitride (Si₃N₄) is one of the outstanding functional materials for many applications because of its good performance in mechanical, chemical, electronic, optoelectronic (with 5.3eV wide band gap), and thermal properties [1]. One-dimensional (1D) Si₃N₄ nanostructures, such as: nanorods [2,3], nanoribbons [4], and nanowires [5,6] have been studied extensively as nanoscale building blocks for potential applications in electronic device fabrication. Silicon nitride nanowires (SiNNWs) have been mostly synthesized via carbothermal reduction and nitriding reaction at temperature higher than 1300 °C [3,7], hot-filament CVD [8], and microwave plasma methods [9]. Despite these synthesis options, there is still a challenge to develop a simple and controllable technique to produce SiNNWs in a large quantity and controlled structures. In this paper, we report a simple method to synthesize SiNNWs of different structures in large quantity by ball-milling and subsequent annealing process.

2. Sample preparation

High-energy ball milling of the pure Si powder (99%, -325 mesh, Sigma-Aldrich) with 4 hardened steel balls in a stainless steel vessel filled with pure N₂, or NH₃, at a pressure of 300 kPa, at room temperature for 150 hours, and followed by a subsequent annealing at 1200 °C for 1 hour in pure N₂ at a flow rate of 50 sccm as a reaction and carrier gas. The annealing was terminated by cooling the furnace to room temperature in the same gases. The structures of the SiNNWs were characterized using X-ray diffraction (XRD) analysis with Co radiation of $\lambda=0.1789\text{nm}$, field emission scanning electron microscope (FESEM) (Hitachi, S-4500 operated at 3kV), high-resolution transmission electron microscope (HRTEM) (Philips, CM 300 operated at 300kV). The chemical compositions were examined using X-ray energy dispersive spectroscopy (EDS) (retractable EDAX SUTW detector attached to the TEM).

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3. Results and Discussion

The TEM image in Fig. 1a shows the typical SiNNWs obtained from the Si powder milled in N_2 after the subsequent annealing. This type of SiNNW is randomly aligned but has a uniform diameter (details given later) and a length of more than $10\ \mu\text{m}$. The structure is very straight without any particle on each nanowire tip. This type of SiNNW has the hexagonal crystal structure of $\alpha\text{-Si}_3\text{N}_4$ as shown by the inserted selected area electron diffraction (SAED) pattern, taken from a group of wires. Each example of this type of SiNNW is a defect-free single crystal with the wire axis parallel to $[10\bar{1}2]$ and wrapped with a thin amorphous surface oxide layer about 7 nm thick, as shown by the lattice image inserted in Fig. 1a.

Changing the milling gas from N_2 to NH_3 with the same subsequent annealing conditions results in different structures of SiNNWs. The TEM image in Fig. 1b shows that this type of SiNNW is also randomly aligned but features a small particle at each nanowire tip with a size 2 – 3 times bigger than the nanowire diameter. The inserted SAED pattern, taken from a group of nanowires, shows mixed diffraction by Si_3N_4 , FeSi_2 , and Fe_2O_3 as well. The inserted lattice image shows the Si-N lattice continuing to the nanowire surface without any thin amorphous surface layer. Each nanowire in this sample milled in NH_3 is also defect-free single-crystal $\alpha\text{-Si}_3\text{N}_4$ with the wire axis parallel to $[1\bar{2}11]$.

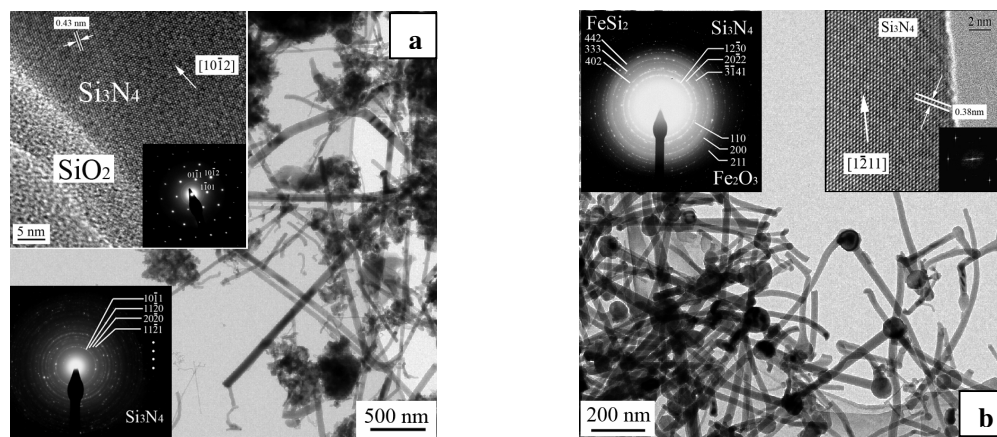


FIG. 1 TEM images of two types of SiNNWs with inserted SAED patterns and the lattice images: (a) milled with N_2 , (b) milled with NH_3 .

Fig. 2a gives the size distributions of diameters for these two types of SiNNWs. The typical diameter is about 10 nm and 25 nm, for the samples milled in N_2 and NH_3 respectively. The unique size in the sharper distribution peak of the sample milled in NH_3 suggests that the size of the tip particle affects the growth process.

Using comparable conditions in TEM, the EDS spectra in Fig. 2b were taken from two single nanowire bodies of each type of SiNNW and a tip head of a SiNNW obtained from NH_3 -milled Si. The spectrum taken from the tip shows Fe, Si, N peaks and a relatively high O peak compared with the spectra taken from the nanowire bodies, consistent with the Fe_2O_3 diffractions marked on the SAED pattern inserted in Fig. 1b.

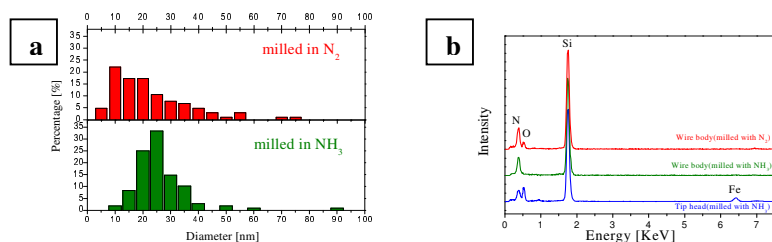


FIG. 2 (a) Size distributions of the diameters for two types of SiNNWs. (b) EDX spectra of two different kinds of SiNNWs.

The growth mechanisms of these two types of SiNNWs are different. As Fig. 3a shows, the pure N₂-milled Si reacted with both N₂, and O₂ during the annealing process to form Si₃N₄ and SiO₂. (O₂ is thought to be present as an impurity in the N₂ gas). The density difference between SiO₂ and Si₃N₄ creates a “sinking cluster” effect [10], so that SiO₂ wraps the outside. Si₃N₄ is able to grow but, being covered by the SiO₂ layer, can only grow in 1D to form SiNNW. This is the oxide-assisted-growth (OAG) mechanism [11].

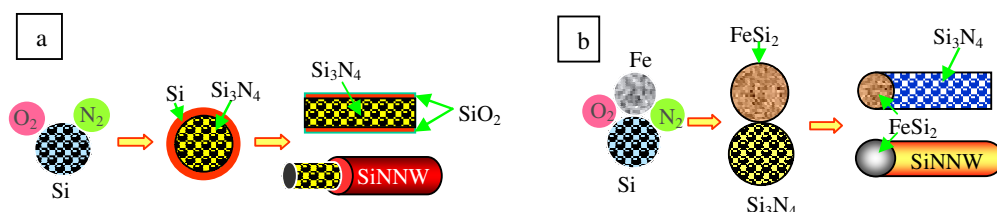


FIG. 3 The growth mechanisms of the two types of SiNNWs: (a) the SiNNWs (milled with N₂) grow by oxide-assisted-growth (OAG) mechanism. (b) the SiNNWs (milled with NH₃) grow by vapor-liquid-solid (VLS) mechanism.

The growth mechanism of the other type of SiNNW produced from NH₃-milled Si is more complicated. This system involved Fe, Si, N and O. This metal alloy played a role as the metal catalyst for the SiNNWs growth. This is the vapor-liquid-solid (VLS) mechanism. As Fig. 3b shows, during the annealing process the Fe particles reacted with O₂ impurities in the carrier gas and Si to form Fe₂O₃ and FeSi₂ respectively. SiO₂ formation is possibly suppressed by H absorbed in the NH₃-milled Si. Si₃N₄ was also included inside the tip head to form a mixed metal alloy.

In summary, single-crystal α -Si₃N₄ SiNNWs have been successfully synthesized in large quantity by ball-milling and annealing method. Changing the milling gas from N₂ to NH₃ results in different SiNNW size, and absence of amorphous SiO₂ surface layer in the N₂ case. The SiNNWs obtained from the N₂-milled Si are grown via OAG mechanism, while those produced from NH₃-milled Si are grown via VLS mechanism. SiNNW formation is facilitated by both the ball milling treatment and the subsequent annealing.

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