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High purity alpha silicon nitride nanowires – synthesis and dielectric properties

T. Xie[*, 1, 2], **Y. C. Wu**[2, 3], **W. P. Cai**[2], and **L. D. Zhang**[2]

[1] Institute of Tribology, Hefei University of Technology, Hefei 230009, P.R. China
[2] Institute of Solid State Physics, Chinese Academy of Science, Hefei 230031, P.R. China
[3] School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, P.R. China

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High purity single crystal alpha silicon nitride (α-Si_3N_4) nanowires were obtained in high yield via a simple vapor phase reaction approach without the presence of catalyst. The produced α-Si_3N_4 nanowires have diameters mostly ranging from 30 to 100 nm and lengths of several hundred micrometers. The nanowires were grown via vapor–solid (VS) mechanism. The room-temperature dielectric properties show that the effective dielectric constants of α-Si_3N_4 nanowires is higher than that of the α-Si_3N_4 micropowders, especially at low frequencies. Analysis of the dielectric properties indicates that the small size effect of nanowires has great influence on the dielectric behavior of the samples.

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1 Introduction

Among the IV-nitrides, Si_3N_4 is the most widely used material, particularly in chemical resistance applications, such as the passive thin film component in various electronic devices (i.e. electronical insulator and diffusion barrier) [1]. The whisker form of Si_3N_4, specifically, enjoys a broad range of applications in ceramic industries due to its high strength, lightweight, good resistant to thermal shock and oxidation [2, 3]. Various process techniques have been developed to obtain Si_3N_4 whiskers since early seventies, which mainly include chemical vapor deposition [4, 5], nitridation of silicon powders [6, 7], carbothermic reduction of a silica-containing compound [8, 9], combustion synthesis [10, 11] and reactive evaporation [12]. However, the diameters of the reported Si_3N_4 whiskers are usually in micron scale. Obtaining uniform Si_3N_4 nanorods or nanowires, which are expected to enhance ductility or superplasticity of ceramic reinforcing materials, remains a challenge. It is not until late nineties, that Si_3N_4 nanowires with diameters less than 40 nm have been reported, for the first time, by using the carbon nanotube confined reaction method [13]. Since then several approaches have been developed to prepare Si_3N_4 nanowires. Carbothermal nitridization has been proved to be a efficient method to produce Si_3N_4 nanowires. SiO_2 nanoparticles with active carbon in flowing N_2 at 1450 °C can produce α-Si_3N_4 nanowires wrapped by Si and SiO_2 [14]. Zhang et al. prepared α-Si_3N_4 nanowires by carbothermal nitridization of SiO_2 xerogel with carbon nanoparticles in its pores at high temperature [15]. It is also reported that the reaction of SiO_2 gel with carbon nanotubes or activated carbon with Fe catalyst in the presence of NH_3 yielded pure α-Si_3N_4 nanowires [16]. Furthermore, α-Si_3N_4 nanowires with an amorphous SiO_2 layer can be obtained by nitriding Si powders or Si/SiO_2 mixture powders [17]. Catalyst assisted synthesis is another effective method to grow Si_3N_4 nanowires, such as using silicon wafer as Si source and Fe or Fe/Ga as catalysts

* Corresponding author: e-mail: txie0001@yahoo.com.cn, Phone: +86 551 290 1359, Fax: +86 551 268 2816

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[18, 19]. In fact, it is now becoming more and more important to seek for a simple and efficient way to synthesize Si_3N_4 nanowires.

With the development of the nanoscience and nanotechnology, the physical properties (such as electric, optic, mechanical properties, etc.) of various nanowires have attracted much attention owing to their unique properties and their potential applications in nanodevices and composites. The Si_3N_4 nanowires have been proved to have a much higher bending strength than the bulk [20]. Without a doubt it is also very important to investigate the dielectric properties of Si_3N_4 nanowires, especially when they are used to fabricate composites for electronic device applications. The previous works about the dielectric properties of Si_3N_4 were mainly focused on those of the Si_3N_4 (or SiN_x) thin films [21–23]. And Wang et al. studied the anomalous dielectric behavior in nanometer-sized amorphous-silicon nitride [24], it was found that the dielectric constant of nanometer-sized amorphous-silicon nitride is much better than that of microsized silicon nitride powders because of their small size effect. However, so far as we know, there has been no report on the dielectric properties of Si_3N_4 nanowires.

In this paper, a catalyst-free vapor phase method was developed to synthesize high-purity α-Si_3N_4 nanowires in high yield, in which the silicon wafer was used as both substrate and silicon source. The great advantages of this method are very simple and efficient. In addition, the dielectric properties of the as-prepared α-Si_3N_4 nanowires were also studied.

2 Experimental

In the experiments, several small pieces of Si(111) wafer (about 8×15 mm) were dipped in ethanol under ultrasonic agitation for 10 min to clean the surfaces and dried, which then were put into a ceramic boat placed in the central region of a ceramic tube in a tubular furnace. Before the experiments, the ceramic tube was flushed with N_2 (purity: 99.999%) for 60 min to eliminate the oxygen in the chamber. The system was rapidly heated to 1200 °C and held at this temperature for 4 hours. During the heating and cooling stage a constant mixture gas flow with NH_3 (purity: 99.999%) at 100 sccm and N_2 (purity: 99.999%) at 20 sccm was maintained. After the system cooled to the room temperature, the ceramic boat was pulled out, it was found that the wool-like products covered the surfaces of the silicon wafers, which were collected for characterizations and measurements. Scanning electron microscope (SEM, JEOL JSM-6700F), transmission electron microscope (TEM, JEM 200CX), high-resolution transmission electron microscope (HRTEM, JEOL-2010) and X-ray diffractometer (XRD, D/MAX-γB with CuK_α radiation) were used to analyze the as-grown products. The dielectric properties of the products were measured by a Dielectric Relaxation Spectrometer (Hioki 3531Z HiTESTER) in the frequency range from 50 Hz to 5 MHz. The samples for the dielectric measurements were small round sheets prepared by pressing the obtained products or the α-Si_3N_4 micropowders (Alfa Aesar, <1 µm, α-Si_3N_4 ≥90%) under 40 MPa.

3 Results and discussions

Figure 1 shows the XRD pattern of the obtained wool-like products. The diffraction peaks can be indexed to α-Si_3N_4 with a hexagonal structure (cell constants: a = 7.75 Å, c = 5.62 Å); no diffraction peaks of other impurities have been found in our samples. It means that the products are high-purity α-Si_3N_4 structures. The typical SEM morphologies of the products are shown in Fig. 2. Figure 2(a) illustrates that uniform α-Si_3N_4 nanowires are formed in high yield and lengths of up to several hundred micrometers. A higher magnification SEM image (Fig. 2(b)) also shows that the nanowires are with smooth surfaces. The diameter distribution of the obtained α-Si_3N_4 nanowires was measured from the SEM images as given in Fig. 3. The α-Si_3N_4 nanowires had a distribution of diameters peaked at 77 nm. Most of the diameters of the nanowires fall in the range of 30–100 nm. The α-Si_3N_4 nanowires were further characterized by TEM and HRTEM. The TEM image (Fig. 4(a)) shows the general morphology of the nanowires: straight, uniform without particles on their surfaces or ends. The high magnification HRTEM image of a individual α-Si_3N_4 nanowire is shown in Fig. 4(b). The lattice plane of (200) with an interplanar spacing

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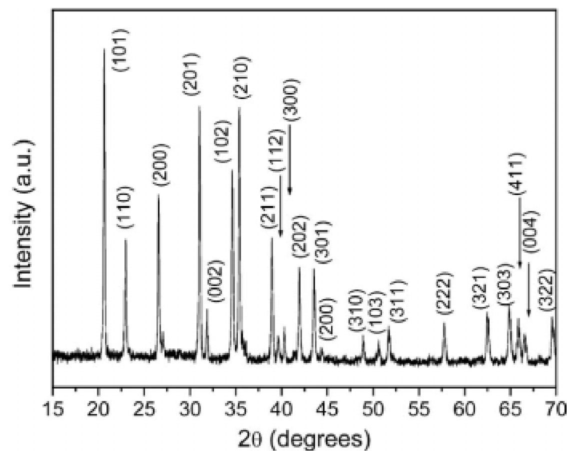

Fig. 1 X-ray diffraction pattern of α-Si_3N_4 nanowires.

of 0.386 nm is clearly displayed. The top inset in Fig. 4(b) is the selected-area electron diffraction (SAED) of the corresponding nanowire, which also shows the crystalline feature of the prepared α-Si_3N_4 nanowire.

The crystalline nanowires formed from vapor phase reactions mainly grow in two ways: the vapor–liquid–solid (VLS) and VS mechanisms. The former is generally based on catalysts, which locate on the top of the nanowires in a liquid-drop state. In our synthesized products, all nanowires' ends are clear; no particles are observed at the ends of the nanowires, which indicated the characteristics of the VS crystal-growth mechanism.

Herein, during the heating process, α-Si_3N_4 nanowires were fabricated on the silicon substrate through a simple chemical reaction as follows:

$$3Si(g) + 4NH_3(g) \rightarrow \alpha\text{-}Si_3N_4(s) + 6H_2(g)\,. \qquad (1)$$

At elevated temperatures, Si atoms were continuously evaporated from the silicon wafer. At the same time the active N atoms were introduced by decomposition of NH_3. Vaporized Si reacted with active N atoms to form Si_3N_4 molecules or clusters, which will then deposit on the surface of the silicon substrate. The deposited Si_3N_4 forms the nuclei for the growth of α-Si_3N_4 nanowires. Subsequently, the post-formed Si_3N_4 molecules or clusters were absorbed on the nuclei to form α-Si_3N_4 nanowires, or on the surface of the silicon substrate to form new nuclei, leading to the growth of new α-Si_3N_4 nanowires.

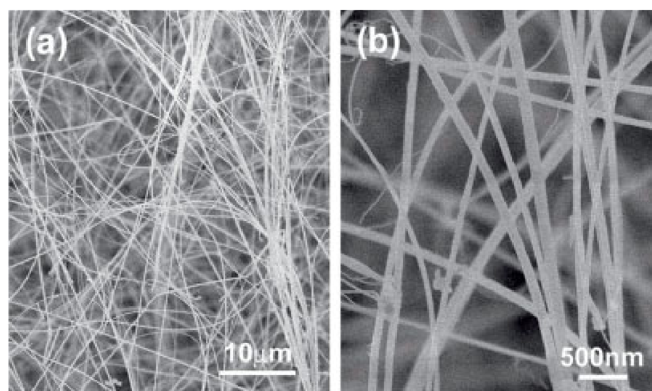

Fig. 2 SEM images of the produced α-Si_3N_4 nanowires: (a) a low magnification image shows the highly yielded nanowires are long and uniform, (b) a higher magnification image illustrates the nanowires are with smooth surfaces.

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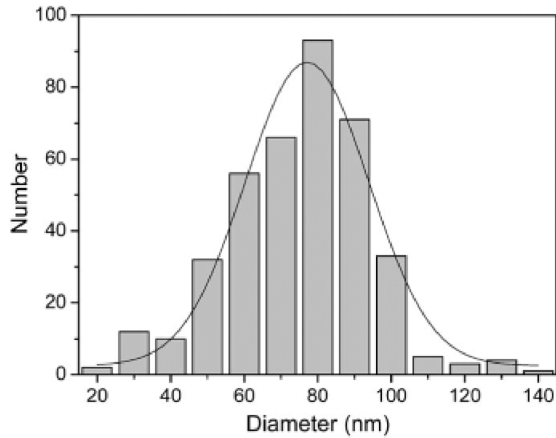

Fig. 3 Distribution of the diameters of as-synthesized α-Si_3N_4 nanowires.

Since Si_3N_4 is one of the important dielectric materials, to investigate the dielectric properties of the α-Si_3N_4 nanowires are certainly necessary and very significant for their eletronic applications, which have been not yet reported before. The relative dielectric constant ε_r of the samples can be obtained from the measured capacitance C according to the following equation:

$$C = \varepsilon_r \varepsilon_0 \frac{S}{d} \tag{2}$$

where ε_0, S and d are the dielectric constant in vacuum, the area and the thickness of the sample, respectively.

However, it should be noted that the existed voids in these compressed samples can not be neglected because their influence on the dielectric constant. In other words, the samples can be regarded as the composites composed of the α-Si_3N_4 component and void component. Therefore, in fact, the effective dielectric constants (ε_{eff}) of the nanowires and the micropowders are differ from those obtained according to Eq. (2). In this case, the effective medium theory for the dielectric function [25, 26] should be employed to get the effective dielectric constants of the samples following a formula listed below [26]:

$$\varepsilon_r = \frac{\varepsilon_{\text{eff}} + 4c\varepsilon_{\text{eff}}(\varepsilon_v - \varepsilon_{\text{eff}})/(2\varepsilon_{\text{eff}} + \varepsilon_v) + 2c^2(\varepsilon_v - \varepsilon_{\text{eff}})^2/(2\varepsilon_{\text{eff}} + \varepsilon_v)}{1 + c(\varepsilon_v - \varepsilon_{\text{eff}})/(2\varepsilon_{\text{eff}} + \varepsilon_v)}, \tag{3}$$

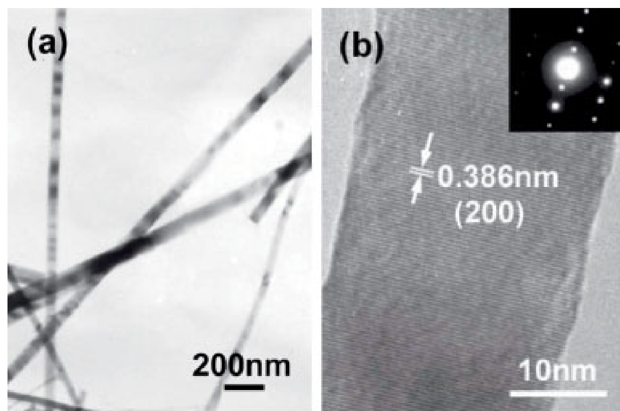

Fig. 4 (a) A typical TEM image of the obtained α-Si_3N_4 nanowires, (b) HRTEM image of a individual α-Si_3N_4 nanowire, interplanar spacing of 0.386 nm is correspondent to the lattice plane of (200). The top inset shows the SAED of the nanowire.

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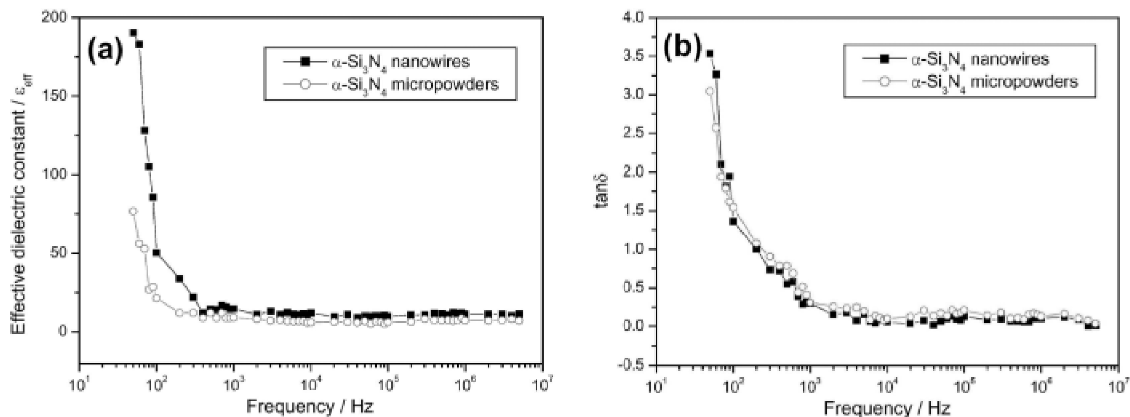

Fig. 5 Dielectric properties of the α-Si_3N_4 nanowire and micropowder samples at room temperature: (a) Frequency dependence of the effective dielectric constant ε_{eff}, (b) frequency dependence of loss angle (tan δ).

where ε_v, c refer to the relative dielectric constant of void, and the volume fraction of void in the sample, respectively. In our work, the void volume fractions of α-Si_3N_4 nanowire and micropowder samples are 9% and 10%, and the ε_v is the relative dielectric constant of air. So we can obtain the ε_{eff} of the tested materials from formulae (2) and (3). The results of ε_{eff} and the recorded dielectric loss (tan δ) at different frequencies at room temperature of the samples are shown in Fig. 5(a) and (b), respectively. It can be seen that the ε_{eff} values of the samples decrease with the increase of frequency (f), similar to the general pattern. The results show that the ε_{eff} of α-Si_3N_4 nanowires is higher than that of α-Si_3N_4 micropowders, especially at low frequencies (Fig. 5(a)). It has been proved that the small size effect of nanostructured materials also greatly affects the dielectric properties of the nanostructured materials by the previous works [24, 27, 28]. Tsu pointed out earlier that a quantum wire will also demonstrate the size-dependent dielectric constant [29]. In fact, the higher dielectric constant of nanostructured materials was mainly contributed to the larger interfaces in the samples, which is also indicated by a study of the dielectric properties of GaN nanowires [30]. More recently, Lewis also confirmed the important effect of interfaces in nanostructured materials on the dielectric behavior of the materials [31]. It is obvious that α-Si_3N_4 nanowires (size: 30–100 nm) have a greater specific surface than α-Si_3N_4 micropowders (<1 μm), namely a larger interface. Therefore, in the nanowire sample, there are much more defects such as vacancies, dangling bonds, etc. A former study showed that there exist many dangling bonds in a compressed sample of nanometer-sized silicon nitride [32]. The interfacial structure is not so dense that the positive and negative charges will easily accumulate at the interfaces to form dipoles in an external electric field. This will lead to the rotation direction polarization. So it is easy to understand that the rotation direction polarization effect plays a very important role in the contribution to higher ε_{eff} of the nanowire sample because of its internal greater interfaces. One the other hand, weak-restricted ions are able to be easily generated owing to a large amount of defects in the interfaces. Accordingly, there may also exist ion relaxation polarization in an external electric field. Figure 5(b) is the curves of tan δ related to frequency. It can be seen that the tan δ differences between the nanowire sample and the micropowder one are very small. It can be found that the most tan δ values of the nanowire sample are a little smaller than that of micropowder sample. The reason is not quite clear yet, which remains to be further studied.

4 Conclusions

In conclusion, the high purity single crystal α-Si_3N_4 nanowires with hexagonal structure have been synthesized in high yield through a simple vapor phase reaction approach without the presence of catalyst. The produced α-Si_3N_4 nanowires have diameters mostly ranging from 30 to 100 nm and lengths of sev-

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eral hundred micrometers. The as-synthesized nanowires grow in terms of VS mechanism. The room-temperature dielectric properties show that the ε_{eff} of α-Si_3N_4 nanowires is higher than that of the α-Si_3N_4 micropowders, especially at low frequencies. Analysis of the tested dielectric properties indicates that the small size effect of nanowires has great influence on the dielectric behavior of the samples.

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