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Preparation of Silicon Nitride Nanowires and Dielectric Properties

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Using carbon nanotubes as template to prepare solid silicon nitride nanowires. The reaction was carried out in ammonia atmosphere. Silicon and SiO_2 were used as starting materials. The structure, phase composition, dielectric properties and oxidation resistance of the sample were investigated. The results showed that the sizes of the nanorods are 60-80 nm in diameter and up to several microns in length. In the products α-Si_3N_4 is the main component. Due to nano-material's quantum size effects, the FTIR spectra of the silicon nitride nanowires have blue shift phenomena. The sample shows good oxidation resistance in high temperature. The dielectric constants decrease with the increasing measuring frequency. The dielectric constants reduced from 9 (10 KHz) to 6.9 (100 MHz) at room temperature.

Key Words: Silicon nitride nanowires, Carbon nanotubes, Precursors, Dielectric properties.

INTRODUCTION

As a covalent material, silicon nitride (Si_3N_4) is recognized as an important candidate in a wide range of industrial applications[1,2], due to its special set of physicochemical properties such as high strength[3], good thermal shock resistance[4], high oxidation resistance and low dielectric constant[5]. All these superior characters has arouse a lot of interest by materials researchers over past years, which makes them become promising candidates for application in many field, *e.g.*, it can serve as molten metal filters[6], soot collectors, heat exchangers[7], catalyst carriers, bioreactors and electronic devices[8]. Most of the researches were carried on the silicon nitride powders and less involved in one dimensional nanomaterials-nitride nanowires. It is remarkable that the silicon nitride nanowires have huge potential value in next generation electronic devices-nanoelectronic devices.

Compared with nanopowders (0 dimensional nanomaterials), the synthesis of one dimensional structure nanomaterials still remain a challenge. Since the discovery of carbon nanotube[9], efforts have been made on synthesis of one dimensional nanoscale materials by using carbon nanotubes as the precursors. Sun *et al.*[10] prepared the diamond nanowires use CNTs-templated method and proposed a model for growth mechanism of nanorods. Han *et al.*[11] reported that they synthesized SiC nanorods in a two-step process involving the generation of SiO followed by reacting with carbon nanotubes under N_2 atmosphere. In this paper, we developed a method to fabricate Si_3N_4 nanowires using carbon nanotubes as the precursor and ammonia as a reaction gas. This method can prepare Si_3N_4 nanowires at low temperature, which make the production low cost at the same time we discussed the dielectric properties of this material.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWCNTs) (96 % purity), diameter 40-60 nm, were supplied by nami gang company, Shenzhen, China; Quartz SiO_2 powder (99.3 % purity, Fine Chemical Plant, Tianjin, China; mean particle size: 0.2 mm); silicon powder (98 % purity, Fine chemical plant, Guangzhou, China; mean particle size: 0.2 mm). These materials were used as starting materials.

Synthesis of silicon nitride nanowires: In the first step, the MWCNTs were purified by concentrated sulfuric acid, the CNTs (1.5 g) were boiled for 24 h in 100 mL 95 wt % H_2SO_4 under refluxing; Then they were washed with water and dried at 80 ºC for 24 h. The mixture of silicon and silicon dioxide powder were spread on the Al_2O_3 boat and covered with as treaded carbon nanotubes to react. The reaction was carried out at 1500 K for 1 h, at the same time ammonia gas was fed into the tube at a flow rate of 50 sccm to maintain the reactant pressure. After reaction for several hours, the specimens were cooled down in nitrogen. Finally a white woollike material formed at the original nanotube bed.

Characterization: X-ray diffraction (XRD) with CuK$_\alpha$ radiation was used at room temperature to identify the phase and the crystal structure. The micro-structure of carbon coated iron nanoparticles was observed by using transmission electron microscope (TEM) (JEM-2010 HR) operating at 200 KV. Q600 DSC/TGA simultaneous, TA companies in the United States was employed to test DSC/TGA. Test conduction: weight between 1.5-2.0 mg, carrier gas is air, heating rate 20 ºC/min, from room temperature to 800 ºC. A Fourier transform infrared spectroscope was used to examine the surface bond of the nanowires. The dielectric constant of the products was measured using multi-frequency meter (HP-4294A).

RESULTS AND DISCUSSION

Phase analysis: Fig. 1 is an XRD pattern of the products, only α-Si_3N_4 phase and α-Si_3N_4 phase are detected by X-ray. The peaks assigned to α-Si_3N_4 (20.5, 26.6 and 30.9º) are stronger than that of α-Si_3N_4, which indicate the products are mainly α-Si_3N_4. At the same time it is observed there is no peak associated with silicon carbide, graphite, or other crystalline in the XRD pattern.

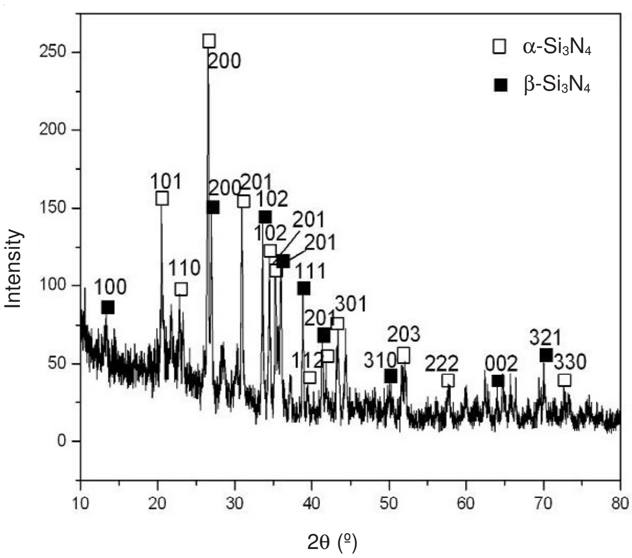

Fig. 1. X-Ray diffraction spectrum of silicon nitride nanowries

Structural and morphology of silicon nitride nanowires: Fig. 2(a) is a TEM micrograph of the origin carbon nanotube, the image shows that the CNTs intertwined each other and with diameters ranging from 40-60 nm several μm in length. Compared with the origin nanotubes, the diameter and length of acid treatment nanotubes is small. Fig. 2(c,d) are the TEM micrographs of the products-silicon nitride nanowires. They are solid other than the hollow core structure of nanotubes. The diameters of the produced nitride nanowires (*ca.* 60-80 nm) are signiûcantly larger than the carbon precursors. Fig. 2(e) shows the growth of nitride nanowires in the carbon nanotube (40-60 nm), it can be seen that nitride start grow at the outlet of the carbon nanotubes. This phenomenon can be expressed simply as follows:

In the reaction process, in the first step, SiO gas was generated *via* the silicon reaction with silica,

$$Si(S) + SiO_2(S) \xrightarrow{\text{High Temp.}} 2SiO(V) \quad (1)$$

Then the generated SiO gas meet the inlet NH_3 gas at the region of carbon nanotubes, then reacted with carbon

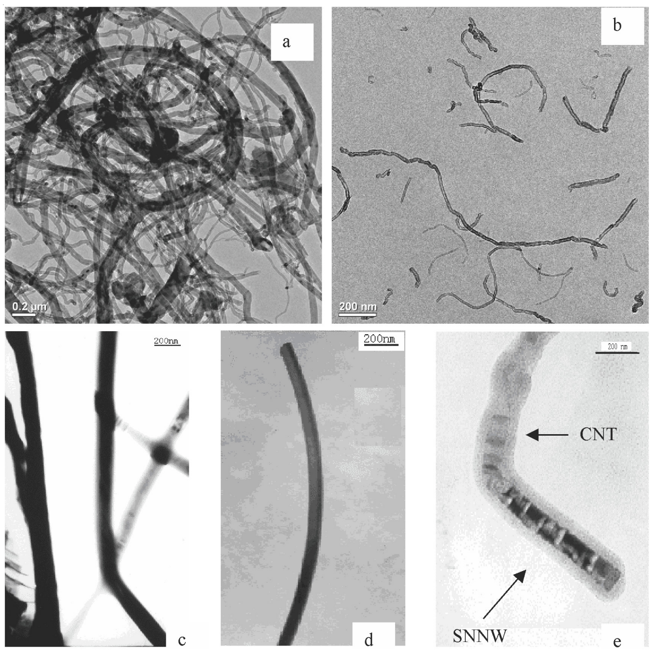

Fig. 2. TEM micrographs of carbon nanotubes and silicon nitride nanowires. (a) original carbon nanotubes; (b) carbon nanotubes treated by acid (c) silicon nitride nanowires; (d) signal silicon nitride nanowire; (e) growth of silicon nitride nanowire)

nanotubes. In a Si-C-N-O-H system, the reaction that could be responsible for the formation of Si_3N_4 is:

$$3SiO(V) + 4NH_3 + 3C(Nanotube) \xrightarrow{\text{High temp.}} Si_3N_4(nanowire) + 3CO(V) + 6H_2 \quad (2)$$

This is the first step to form Si_3N_4 and in this stage carbon nanotubes are carbon. In the second step, another carbon source of CO gas which generated from reaction (2). That means the above reaction along with the reaction

$$3SiO(V) + 4NH_3(V) + 3CO(V) \xrightarrow{\text{High temp.}} Si_3N_4(nanowire) + 3CO_2(V) + 6H_2 \quad (3)$$

The new generated Si_3N_4 deposited around the Si_3N_4 nanowires produced in reaction (2), this explained why the diameter of nitride nanowires larger than that of carbon precursors. The carbon nanotubes act as a template in the reaction to confine the reaction in a local space around carbon nanotube. After the nanotube is exhausted, CO continue react to form Si_3N_4 around the initial nanowires.

FTIR spectra of silicon nitride nanowires: The FTIR spectra of the silicon nitride nanowires are shown in Fig. 3. The sample has three main peaks., the peak at 492.8 cm^{-1} is stretching motion of N-Si bonds, the peak at 1644.7 cm^{-1} is exural vibration of the N-Si bonds, the Si=O stretching bond is observed near 998 cm^{-1}. Comparison with block nitride peaks at 481.31, 989 and 1599 cm^{-1}. The infrared spectrum of nano-structure materials has a blue shift phenomena. The reason is that the nano-material's quantum size effects lead to blue shift. Nano-materials have great surface area, surface atoms will have defects and lattice distortion, the bond length of surface atoms different to the body atoms, which makes the nanowire's blue shift of infrared absorption spectrum.

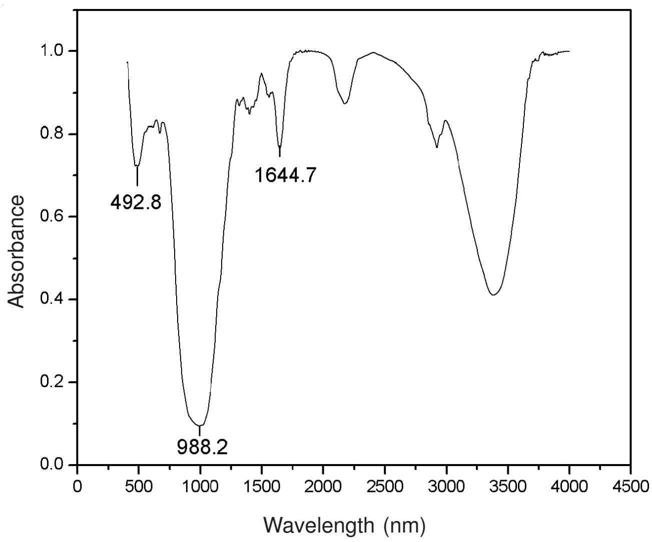

Fig. 3. FTIR spectra of the silicon nitride nanowire

Thermal stability of silicon nitride nanowires: A DSC/TG is employed in order to examine the antioxidant ability of the products, as it can be seen from the Fig. 4 can be divided into two stages when the temperature increase. From room temperature to 350 ºC thermal gravity decreases *ca.* 1 % with increasing of temperature. It is suggested that this weight loss is due to oxidation of unreacted carbon. After that with the increase of temperature the weight of sample only increase 0.5 %, which suggests that little of nitride silicon oxide at this stage.

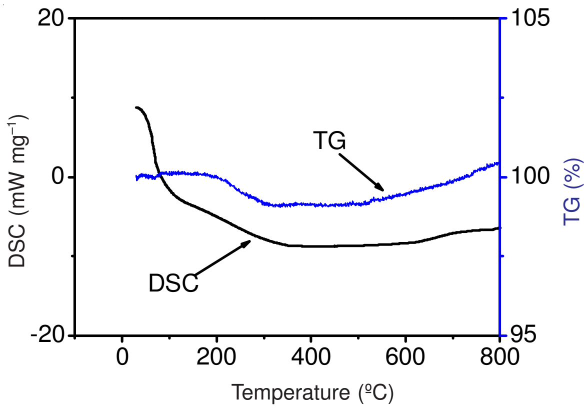

Fig. 4. DSC /TG curve of silicon nitride nanowire

Dielectric constant: Being a convention electronic materials[12], it is useful to test the dielectric constant (ε_r) of silicon nitride nanowires. The sample were measured at 10 kHz, 100 kHz, 1 MHz, 10 MHz and 100 MHz at ambient temperature (Fig. 5). The results showed that the sample have a decreasing tendency of the dielectric constants with increasing of measuring frequency, even at a microwave frequency. The dielectric constants reduced from 9 (10 KHz) to 6.9 (100 MHz).

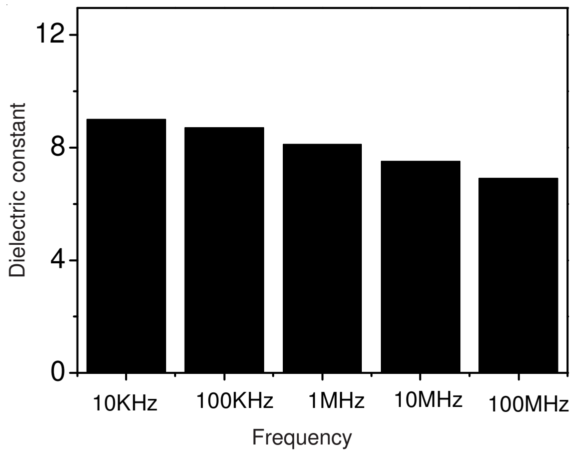

Fig. 5. Dielectric constant of sample measured at 10 kHz, 100 kHz, 1 MHz, 10 MHz and 100 MHz, respectively

Conclusion

Silicon nitride nanowires are fabricated using carbon nanotubes as precursors and the samples mainly are α-Si_3N_4 and β-Si_3N_4, α-Si_3N_4; different from the nanotubes, the silicon nitride nanowires are solid materials. At the same time the diameter of nitride is larger than the nanotubes. The sample shows good oxidation resistance, only a little of the nitride can be oxidized in high temperature. The dielectric properties of silicon nitride nanowires were measured at different frequencies. The results showed the decreasing tendency of dielectric properties with the increasing measuring frequencies.

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